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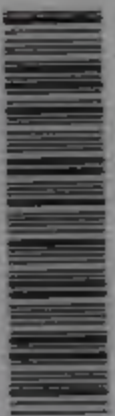
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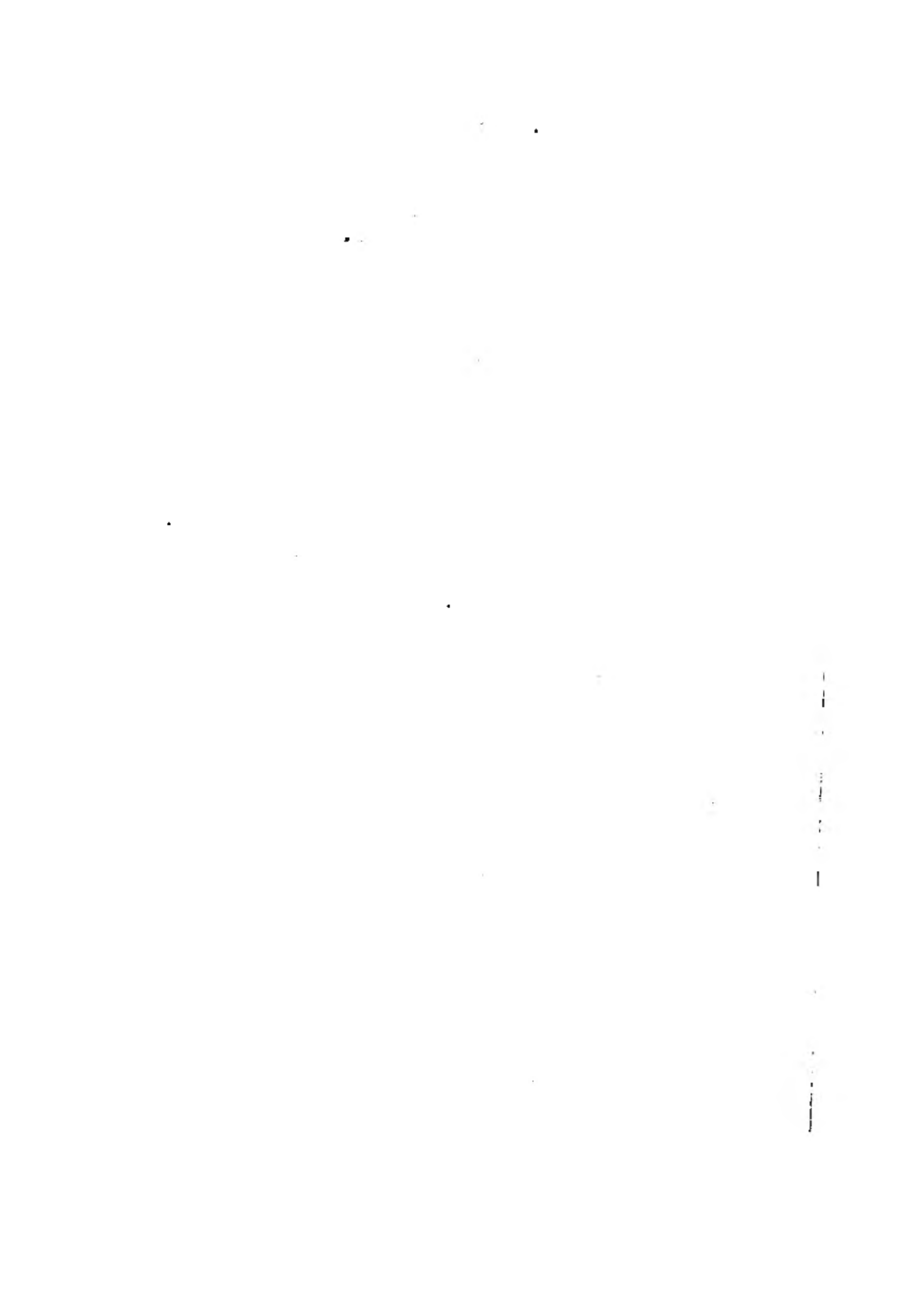
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AN INTRODUCTION TO THE STUDY  
OF THE  
COMPOUNDS OF CARBON  
OR  
ORGANIC CHEMISTRY

IV

IRA REMSEN

*REVISED AND ENLARGED  
WITH THE COLLABORATION OF THE AUTHOR*

BY

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D. C. HEATH & CO., PUBLISHERS  
BOSTON NEW YORK CHICAGO



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**By IRA REMSEN**

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**YANSEN**

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## PREFACE

QUOTING from the preface to the first edition: "This book is intended for those who are beginning the subject. For this reason, special care has been taken to select for treatment such compounds as best serve to make clear the fundamental principles. General relations as illustrated by special cases are discussed rather more fully than is customary in books of the same size; and, on the other hand, the number of compounds taken up is smaller than usual. The author has endeavored to avoid dogmatism, and to lead the student, through a careful study of the facts, to see for himself the reasons for adopting the prevalent views in regard to the structure of the compounds of carbon. Whenever a new formula is presented, the reasons for using it are given so that it may afterward be used intelligently. It is believed that the book is adapted to the needs of all students of chemistry, whether they intend to follow the pure science, or to deal with it in its applications to the arts, medicine, etc. It is difficult to see how, without some such general introductory study, the technical chemist and the student of medicine can comprehend what is usually put before them under the heads of 'Applied Organic Chemistry' and 'Medical Chemistry.'"

These words apply to the present edition. For some time I have been aware that the book needed a thorough overhauling, but one thing and another prevented me from undertaking the work. Finally, I decided to ask Dr. W. R. Orndorff of Cornell University to join me. He consented, and the many additions and corrections that have been made are largely due to him. I have great confidence in his accuracy and thoroughness, and I am sure that these qualities will be evident to those who may examine and use this new edition.

Organic chemistry has come very much to the front in the last few years, and I suppose it is true that for one who studied

the subject at the time the book was written a hundred study it now. Most of these are in the early stages of their study, and I have had them principally in mind. At the same time a good deal of new material has been introduced which will, I believe, be helpful to those who have passed beyond the first stage.

I make no apology and offer no explanation. I do not see how any one can acquire a working knowledge of the subject without learning about compounds and a good many of them. The acquisition of this knowledge is much facilitated by a study of the structure of the compounds. Organic chemistry is to a large extent structural chemistry. Without this aid the subject would be confusion worse confounded. Structural formulas play somewhat the same part as mathematics in some related subjects. We do not, however, need to be told that they are not the end. Properly used they reveal the inner nature of the things they represent, and they are therefore of great value.

One change has been made that will be noted at once. The descriptions of laboratory experiments have been omitted. I am informed that in most laboratories special manuals designed for that purpose have come into use, and it is clear therefore that it is not necessary to include this matter in the book. Professor Orndorff long ago prepared such a laboratory manual and a new edition will appear at about the same time as this book.

Cross references abound throughout the text and appear in parenthesis in heavy-faced type.

IRA REMSEN.

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## ORGANIC CHEMISTRY



# CHEMISTRY OF THE COMPOUNDS OF CARBON

## CHAPTER I

### INTRODUCTION

IN studying the compounds of carbon, one cannot fail to be struck by their large number, and by the ease with which they undergo change when subjected to various influences. Mainly on account of the large number (200,000), though partly on account of peculiarities in their chemical conduct, it is customary to treat of these compounds by themselves. At first, *Chemistry* was divided into *Inorganic* and *Organic Chemistry*, as it was believed that there were fundamental differences between the compounds included under the two heads. Those compounds which form the mineral portion of the earth's crust were treated under the first head, while those which were found ready formed in the organs of plants or animals were the subject of organic chemistry. It was believed that, as the organic compounds are elaborated under the influence of the life process, there must be something about them which distinguishes them from the inorganic compounds in whose formation the life process has no part. Gradually, however, this idea has been abandoned; for, one by one, many of the compounds which are found in plants and animals have been made in the chemical laboratory, and without the aid of the life process. The first instance of the artificial preparation of an organic compound was that of urea, a constituent of the urine. This substance was obtained by Wöhler in 1828 by the action of a solution of

ammonia on lead cyanate (then considered to be an inorganic compound, as it was made in the laboratory). Up to the time of Wöhler's discovery, the formation of urea, like that of other organic compounds, was thought to be necessarily connected with the life process; but it was thus shown that urea could be formed without the intervention of life. Afterward, it was shown that potassium cyanide can be made by passing nitrogen over a heated mixture of carbon and potassium carbonate; and, as potassium cyanate can be made from the cyanide by oxidation, and is easily converted into lead cyanate, it follows that urea can be made from the elements. Finally, in 1853, Berthelot succeeded in effecting the synthesis of the fats. Since that time, every year has witnessed the artificial preparation, by purely chemical means, of compounds of carbon which are found in the organs of plants and animals.

It hence appears that the formation of the compounds of carbon is not dependent upon the life process; that they are simply chemical compounds governed by the same laws that govern other chemical compounds; and the name, *Organic Chemistry*, signifying, as it does, that the compounds included under it are necessarily related to the organism, is misleading. Organic chemistry is nothing but the Chemistry of the Compounds of Carbon. It is not a science independent of inorganic chemistry, but is just as much a part of chemistry as the chemistry of the compounds of sodium, or of the compounds of silicon, etc.

The name *Chemistry of the Compounds of Carbon* has been objected to as being too broad. Strictly speaking, this title includes the carbonates, and it is customary to treat of these widely distributed substances under the head of Inorganic Chemistry. Most books on Inorganic Chemistry also deal with some of the simpler compounds of carbon, such as the oxides, cyanogen, marsh gas, etc., because they are of such common occurrence and so important that it is essential that the student should have a knowledge of them as soon as possible.

**Sources of Organic Compounds.** — Many organic compounds are obtained from plants and animals. Thus, sugar from the sugar cane, the sugar beet, or the maple tree; starch from

Indian corn or the potato; sugar of milk, casein, and fat from milk; albumin from the egg; urea, uric acid, and hippuric acid from the urine; tartaric acid from grapes; citric acid from lemons and grape fruit; malic acid from apples; gallic acid and tannin from nut galls; caffeine from coffee or tea; theobromine from cocoa; and cellulose from wood or cotton. The alkaloids are obtained from plants, quinine from cinchona bark; strychnine from *nux vomica*; morphine from the poppy; and nicotine from tobacco. Various coniferous trees, such as the pine, yield turpentine and, when this is distilled, it gives the volatile oil of turpentine and a residue called rosin. The essential oils also furnish a large number of important substances. Thus, the oil of cloves contains eugenol; the oil of anise seed, anethol; the oil of sassafras, safrol; and the oil of eucalyptus, eucalyptol. Gum camphor, used in such large quantities in making celluloid, is obtained from the camphor tree (*Laurus camphora*), which is now being successfully grown in Florida. Rubber or caoutchouc, of such great importance nowadays, is obtained from the rubber tree (*Hevea brasiliensis*), indigenous to Brazil, and from the same tree, cultivated on large plantations in Ceylon and other tropical countries. The fats are obtained from both animal and vegetable sources. The solid fats, called tallow, from beef and mutton fat; lard from hog fat; cotton seed oil from cotton seed; olive oil from olives; and linseed oil from flax seed.

Many organic compounds are obtained by fermentation. Thus the fermentation of sugar solutions by yeast gives alcohols. When alcoholic solutions, such as cider or wine, are exposed to the air, they ferment and become vinegar, owing to the conversion of the alcohol into acetic acid, by the action of the *bacterium aceti*. Milk exposed to the air becomes sour because of the transformation of the sugar of milk into lactic acid by the lactic acid ferment. Another form of lactic acid occurs in flesh and hence is called sarcolactic acid.

A great many organic compounds are now obtained from the by-products of some chemical industry, and the utilization of these by-products (formerly thrown away or burned as fuel) has become an important source of wealth. Wood is distilled



for the purpose of making charcoal (for use in the manufacture of gunpowder and as a fuel) and formerly the volatile products were lost. They are now condensed and from the distillate wood alcohol, acetone, and acetic acid are obtained. Bituminous coal is distilled in closed retorts for the purpose of making coal gas for illuminating purposes. One of the by-products is coal tar. From this more organic substances are now made than are obtained from all other sources combined. Dyes, perfumes, flavoring essences, antiseptics, medicinal remedies and the modern high explosives, such as picric acid and TNT, are some of the organic compounds obtained from this source and hence called coal tar products. In the coking of coal to make coke, for use in the manufacture of iron and steel, the volatile products, formerly burned, are now recovered and converted into valuable organic compounds. Indeed, many of the coal tar products are not now made from coal tar, but from the by-products of the coking ovens. Petroleum consists almost entirely of compounds of carbon and hydrogen, and from it by distillation are obtained gasoline, kerosene, vaseline, paraffin wax, and the lubricating oils. Bones are distilled for the purpose of making boneblack or ivory black used as a pigment. The volatile products when condensed are known as bone oil, from which are obtained a large number of organic compounds containing carbon, hydrogen, and nitrogen and having basic properties like ammonia. Certain of these basic compounds, found in bone oil and also in coal tar, have been obtained from some of the alkaloids, and some of the alkaloids have already been made from these constituents of bone oil. From the compounds obtained from the above sources most of the organic compounds are now made in the laboratory or in the factory.

**Purification of organic compounds.** — Before the natural compounds of carbon can be studied chemically, they must be freed from foreign substances; and before the constituents of the complex mixtures, petroleum, coal tar, and bone oil can be studied, they must be separated and purified. The processes of separation and purification are, in many cases, extremely difficult. If the substance is a solid, different methods

may be used, according to the nature of the substance. Crystallization is more frequently made use of than any other process. This is well illustrated, on the large scale, in the refining of sugar, which consists, essentially, in dissolving the raw sugar in water, filtering through bone black, which absorbs coloring matter, and then evaporating down to crystallization. When two or more substances are found together, they may, in many cases, be separated by what is called *fractional crystallization*. This consists in evaporating the solution until, on cooling, a comparatively small part of the substance is deposited. This deposit is filtered off, and the solution further evaporated, when a second deposit is obtained, and so on to the end. The successive deposits thus obtained are then recrystallized, each separately, until, finally, some of the deposits are found to be homogeneous.

The chief solvents used are water, alcohol, ether, petroleum ether, benzene, and carbon bisulphide, alcohol being the one most generally applicable.

In the case of liquids, the process of distillation is used. The forms of apparatus and mode of procedure are described in various laboratory manuals,<sup>1</sup> and the subject of distillation is treated fully in a recent book to which reference is here made.<sup>2</sup>

For the separation of liquids of different boiling points, the process of *fractional* or *partial distillation* is much used. When a mixture of two or more liquids of different boiling points is boiled, it will be noticed generally that the boiling point gradually rises from that of the lowest boiling substance to that of the highest. Thus, ordinary alcohol boils at  $78^{\circ}$ , and water at  $100^{\circ}$ . If the two are mixed and the mixture distilled, it will be found that it begins to boil at  $78^{\circ}$ , but that very little passes over at this temperature. Gradually, as the distillation proceeds, the temperature indicated by the thermometer becomes higher and higher, until at last  $100^{\circ}$  is reached, when all distils over. Now the distillates obtained at the different tempera-

<sup>1</sup> *A Laboratory Manual of Organic Chemistry*, by W. R. Orndorff (D. C. Heath & Co.).

<sup>2</sup> *Distillation: Principles and Processes*, by Sidney Young (Macmillan).

tures differ from each other in composition. Those obtained at the lower temperatures are richer in alcohol than those obtained at the higher temperatures, but none of them contains pure alcohol or pure water. In order to separate the two, therefore, we must proceed as follows: A number of clean, dry flasks are prepared for collecting the distillates. The boiling is begun, and the point at which the first drop of the distillate appears in the receiver is noted. That which passes over while the mercury rises through a certain number of degrees (3, 5, or 10, according to the character of the mixture) is collected in the first flask. The receiver is then changed, without interruption of the boiling, and that which passes over while the mercury rises through another interval equal to the first is collected in the second flask. The receiver is again changed, and a third distillate collected; and so on, until the liquid has all been distilled over. It has thus been separated into a number of fractions, each of which has passed over at a different temperature. In the case of alcohol and water, for example, we might have collected distillates from  $78^{\circ}$  to  $83^{\circ}$ , from  $83^{\circ}$  to  $88^{\circ}$ , from  $88^{\circ}$  to  $93^{\circ}$ , from  $93^{\circ}$  to  $98^{\circ}$ , from  $98^{\circ}$  to  $100^{\circ}$ . Now a clean distilling flask is taken, and into this the first fraction is poured. This is distilled until the thermometer marks the upper limit of the original first fraction ( $83^{\circ}$ ), the new distillate being collected in the flask which contained the first fraction. When this upper limit is reached, the boiling is stopped. Some of the liquid is left in the distilling flask. That is to say, assuming that in the first distillation the first fraction was collected between  $78^{\circ}$  and  $83^{\circ}$ , on boiling this fraction the second time it will not all come over between these points; when  $83^{\circ}$  is reached some will be left in the flask. The second fraction is now poured into the distilling flask through a funnel tube, and the boiling is again started. Of the second fraction, a portion will pass over below the point at which it began to boil ( $83^{\circ}$ ) when first distilled. Collect in the proper flask, and continue the boiling until the thermometer marks the highest point of the fraction last introduced, changing the receiver whenever the indications of the thermometer require it. Now stop the

Coal tar. by-product when bituminous coal is  
distilled to make illuminating gas.

## DETERMINATION OF THE BOILING POINT

7

boiling, and pour in fraction No. 3, and so on until all the fractions have been subjected to a second distillation. On examining the new fractions, it will be found that the liquid tends to accumulate in the neighborhood of certain points corresponding to the boiling points of the constituents of the mixture. The distilling flask is now cleaned, and the whole process repeated. A further separation is thus effected. By continuing the distillation in this way, pure substances can, in many cases, eventually be obtained. In many cases perfect separation cannot be effected by means of fractional distillation; as, for example, in the case of alcohol and water. But still it is valuable, even in such cases, as it makes it possible to purify the substances, at least partially.

Various devices have been introduced for the purpose of rendering the process of fractional distillation more rapid and more efficacious. One of these that has been extensively used with good results is the Hempel distilling tube. This is "a wide vertical tube, filled with glass beads of special construction, and constricted below to prevent the beads falling out. A short, narrower, vertical tube with side delivery tube is fitted by means of an ordinary cork into the wide tube."<sup>1</sup> The wide vertical tube is fitted into the stopper of the distilling flask.

The best examples of distillation carried on on the large scale are those of alcohol and petroleum. Probably the best example of fractional distillation is that of the light oil obtained from coal tar. This process is carried on in the so-called "column stills," of which there are several varieties. Some of them are very efficient.<sup>1</sup>

**Determination of the boiling point.**—In dealing with liquids, it often is extremely difficult to tell whether they are pure or not. The first and most important physical property utilized for this purpose is the boiling temperature, commonly called the *boiling point*. This is determined by means of the apparatus used for distilling, such as is described above. The temperature noted on the thermometer when the liquid is boiling is the boiling point. When great accuracy is required, the point observed

<sup>1</sup> See *Distillation: Principles and Processes*, by Sidney Young (Macmillan).

directly must be corrected, in consequence of the expansion of the glass and the cooling of that part of the column of mercury which is not in the vapor. Full directions for making these corrections can be found in larger books. A pure chemical compound always has a constant boiling point under the same barometric pressure. On the other hand, a constant boiling point does not necessarily indicate a pure compound.<sup>1</sup>

**Determination of the melting point.**<sup>2</sup> — Just as the boiling point is a very characteristic property of liquids, so the melting point is an equally characteristic property of many solid substances. If a substance begins to melt at a certain temperature, and does not melt completely at that temperature, it is, in all probability, impure. By means of the melting point minute quantities of impurities, which might readily escape detection by other means, are often found. In dealing with the compounds of carbon, determinations of melting points are very frequently made. A pure chemical compound has a constant melting point. The determination is made as follows: Small tubes are prepared by heating a piece of ordinary soft glass tubing of 4<sup>mm</sup> to 5<sup>mm</sup> diameter, and drawing it out. If the parts are drawn apart about 12<sup>cm</sup> to 15<sup>cm</sup>, two small tubes may be made from the narrowed portion by melting together in the middle, and then filing off each piece where it begins to grow wider near the large tube. These small tubes must have thin walls, and be of such internal diameter that an ordinary pin can be introduced into them. A small quantity of the substance to be tested is placed in one of the tubes, enough to make a minute column of about 5<sup>mm</sup> in height. The tube containing the substance is fastened to a thermometer by means of a small rubber band or by fine platinum wire. The band is placed near the upper part of the tube, and the lower part of the tube, containing the substance, is placed against the bulb of the thermometer. The thermometer bulb is now immersed

<sup>1</sup> See *Distillation: Principles and Processes*, by Sidney Young (Macmillan).

<sup>2</sup> For details in determining melting points and boiling points, see *A Method for the Identification of Pure Organic Compounds*, by J. P. Mulliken.

in a tube containing pure sulphuric acid. The sulphuric acid is gently heated by a small flame until the substance melts.

A convenient form of apparatus for determining melting points is the Thiele tube modified by Dennis.<sup>1</sup>

It does not necessarily follow that, if a substance has a sharp melting point, it is pure. It may be a eutectic mixture which has a constant melting point. In order to avoid this error, the substance should be crystallized from a number of different solvents, using solvents as unlike each other as possible. If the melting point remains constant from all these solvents, it is practically certain that the substance is pure, for it is extremely unlikely that the two components of a eutectic mixture would have the same solubility in all the solvents. It is much more likely that one mixture would crystallize from one solvent and another from another solvent, that is, that the melting point would change with the solvent. If a substance has a constant boiling point and also a sharp and definite melting point, there is no doubt that it is pure.

**Analysis.** — Having purified the compounds, the next step is to determine their composition. A comparatively small number of the compounds ordinarily met with consist of carbon and hydrogen only; the largest number consist of these two elements together with oxygen; many contain carbon, hydrogen, oxygen, and nitrogen. But, in the derivatives of the fundamental compounds, all other elements may occur. Thus the hydrogen may be partly or wholly replaced by chlorine, bromine, or iodine, as in the so-called substitution products; and any metal may occur in the salts of the acids of carbon. The estimation of carbon and hydrogen is the principal problem in the analysis of the compounds of carbon. This is effected by what is known as the *combustion process*. A known weight of the substance is completely burned in oxygen, the carbon being thus converted into carbon dioxide, and the hydrogen into water. These two products are collected, the water in a tube containing sulphuric acid, the carbon dioxide in a

<sup>1</sup> See L. M. Dennis, *Journal of Industrial and Engineering Chemistry*, Vol. 12, p. 366.

solution of potassium hydroxide, and weighed. From the weights of the products the weights of carbon and hydrogen and the percentages are calculated. The percentages are added together and the sum subtracted from 100. The difference is the percentage of oxygen, provided the substance contains only these elements.

A detailed description of the apparatus and of the method of procedure need not be given here, as they can be found in any book on analytical chemistry. A brief description, however, may not be out of place. The combustion is effected in a hard-glass tube which is heated by means of a gas or electric furnace constructed for the purpose. Ordinarily, the substance is placed in a narrow porcelain or platinum vessel, called a *boat*, which is introduced into the combustion tube filled with granulated copper oxide. The tube is then connected with (1) a U-tube containing sulphuric acid; (2) a set of bulbs containing a solution of potassium hydroxide, and constructed so as to secure thorough contact of the passing gases with the solution; and (3) a small U-tube containing sulphuric acid. During the combustion, a current of pure dry oxygen is passed through the tube; and, finally, the oxygen is displaced by air. The method at present used was devised by Liebig. It has contributed very greatly to our knowledge of the compounds of carbon.

N  
Two methods are in common use for the estimation of nitrogen in carbon compounds. The first is known as the absolute method. This consists in oxidizing the substance by copper oxide; decomposing, by means of a roll of heated metallic copper, any oxides of nitrogen which may have been formed, and collecting the nitrogen. The volume of the nitrogen thus obtained is measured, and its weight calculated. The chief difficulty in this method consists in removing all the air contained in the apparatus before the combustion is made. The simplest way is to displace the air by passing pure carbon dioxide through the apparatus until the gas that passes out is completely absorbed by caustic potash. The combustion is then made by heating the tube containing the substance and copper oxide and a layer of copper foil or wire gauze; and, finally, carbon dioxide is

again passed through at the end of the operation. The only three gases that can be present, assuming that the substance contained nothing but carbon, hydrogen, oxygen, and nitrogen, are carbon dioxide, water vapor, and free nitrogen. The water vapor is, of course, condensed, and the carbon dioxide is absorbed by passing the gases through a solution of potassium hydroxide, leaving the nitrogen thus alone.

The method now most extensively used is that devised by Kjeldahl. This consists in oxidizing the substance by heating it with concentrated sulphuric acid, potassium sulphate, and a little copper sulphate. By this means all the nitrogen contained in the substance under examination is converted into ammonia, which, of course, unites with the sulphuric acid. The ammonia is set free by the addition of sodium hydroxide, and is estimated by absorption in standard acid.

In regard to the estimation of other constituents of carbon compounds, it need only be said that in most cases it is necessary to get rid of the carbon and hydrogen by some oxidizing process before the estimation can be made. Thus, in estimating sulphur, it is customary to fuse the substance with potassium nitrate and hydroxide, when the carbon, hydrogen, and sulphur are oxidized, and the sulphur, in the form of potassium sulphate, can be estimated in the usual way.

**Formula.** — The deduction of the formula of a compound from the results of the analysis involves two steps. The first is a matter of simple calculation. It is assumed that students who use this book are already familiar with the method of calculating the formula from the analytical results; but an example will, nevertheless, be given. Suppose that the analysis has shown that the substance contains 52.18 per cent carbon, 13.04 per cent hydrogen, and 34.78 per cent oxygen. To get the atomic proportions, divide the figures representing the percentages of the elements by the corresponding atomic weights. We have thus: —

	PERCENTAGE		AT. WT.		RELATIVE NO. OF ATOMS	
C	52.18	÷	12	=	4.35	— 2
H	13.04	÷	1	=	13.04	— 6
O	34.78	÷	16	=	2.17	— 1



That is to say, accepting the atomic weights 12 for carbon and 16 for oxygen, the simplest figures representing the number of atoms of the three elements in the compound are 2 for carbon, 6 for hydrogen, and 1 for oxygen. According to this, the simplest formula that can be assigned to a substance giving the above results on analysis is  $C_2H_6O$ . But the formula  $C_4H_{12}O_2$  is equally in accordance with the analytical results, and we can only decide between the two by determining the *molecular weight*.

Every chemical formula is intended to represent the relative weight of the molecule of a compound and the composition of the molecule. Our conception of the relative weights of molecules is based almost exclusively on Avogadro's law, according to which equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. Hence, by comparing the weights of equal volumes of compounds in the form of gas or vapor, figures are obtained that bear to one another the same relations as the weights of the molecules.

The molecular weight of a gas is the weight of any volume of that gas as compared with the weight of the same volume of some standard gas, both being measured under the same conditions of temperature and pressure. The standard generally used is oxygen, and its molecular weight has been shown to be twice as great as its atomic weight, that is to say, 32. The volume occupied by 32 grams of oxygen at  $0^\circ$  and  $760^{\text{mm}}$  is 22.4 liters. It follows, therefore, from Avogadro's law, that *the weight of 22.4 liters of any gas or vapor measured at  $0^\circ$  and  $760^{\text{mm}}$  will be the molecular weight of that gas or vapor*.

It need hardly be said that it is not necessary to weigh 22.4 liters of the gas. Any volume may be weighed and the necessary corrections made for temperature, pressure, and volume. As this subject is fully dealt with in courses in Inorganic Chemistry which always precede the courses in Organic Chemistry, it need not be further discussed here.

To illustrate by means of a compound whose atomic relations have been found by analysis to be represented by the formulas

$C_2H_6O$ ,  $C_4H_{12}O_2$ ,  $C_6H_{18}O_3$ , or some higher multiple of  $C_2H_6O$ . Suppose that, when this compound is converted into vapor, the weight of 22.4 liters at  $0^\circ$  and  $760^{mm}$  is found to be 46.2 grams. Then the molecular weight of the compound is 46, or the formula is  $C_2H_6O$ , and not  $C_4H_{12}O_2$ , nor any higher multiple of  $C_2H_6O$ .

The molecular weight of an acid can be determined by analyzing its salts. To illustrate this take acetic acid. This is a monobasic acid, that is to say, it gives but one silver salt and hence contains but one hydrogen atom replaceable by a metal. Now analysis of acetic acid shows that it has the composition represented by the formulas  $CH_2O$ ,  $C_2H_4O_2$ ,  $C_3H_6O_3$ , etc. The analysis of the silver salt shows that it contains 64.67 per cent silver, hence it must be represented by the formula  $C_2H_3O_2Ag$  and not  $CHOAg$ , and the molecular formula of acetic acid is therefore  $C_2H_4O_2$ , and not  $CH_2O$ .

Two other methods of determining molecular weights, the freezing point and boiling point methods, are now much used. By means of these methods the molecular weights of substances which cannot be vaporized without undergoing decomposition (such as sugar) can also be determined. They are so simple and convenient that they have almost entirely supplanted the other methods.<sup>1</sup>

**Structural formula.** — The formulas  $C_2H_6O$ ,  $C_2H_4O_2$ ,  $CHCl_3$ , etc., tell us the composition of the three compounds represented, and also the weights of their molecules. In studying the chemical conduct of these compounds, their decompositions, and the modes of preparing them, we become acquainted with many facts which it is desirable to represent by means of the formulas. Thus, for example, only one of the four atoms of hydrogen represented in the formula of acetic acid,  $C_2H_4O_2$ , can be replaced by metals. It plainly differs from the three remaining hydrogen atoms, and it is natural to conclude that it is held in the molecule in some way different from the other three. We may, therefore, write the formula  $H.C_2H_3O_2$ , which is intended to call attention to this difference. By further

<sup>1</sup> For details of these methods see *Practical Physical Chemistry* by A. Findlay, 3d edition, 1917.

study of acetic acid, we find that the particular hydrogen, which gives to it its acid properties, and which, in the above formula, is written by itself, is directly connected with oxygen. It can be removed with oxygen by simple reactions, and the place of both taken by one atom of some other element, as, for example, chlorine. Thus, when acetic acid is treated with phosphorus trichloride it is converted into acetyl chloride:—



The result of the action is the direct substitution of one atom of chlorine for one atom of hydrogen and one atom of oxygen in acetic acid, a fact which points to an intimate connection between the hydrogen and oxygen in the acid. Further, when acetyl chloride is treated with water, acetic acid is regenerated, hydrogen and oxygen from the water taking the place of the chlorine, as represented in this equation:—



From facts of this kind the conclusion is drawn that in acetic acid hydrogen and oxygen are *connected*, or, as it is said, *linked together*; and this conclusion is represented in chemical language by the formula  $\text{C}_2\text{H}_3\text{O.OH}$ , which may serve as a simple illustration of what are called *structural* or *constitutional* formulas. It does not, however, tell the whole story and may therefore be called a partial structural formula. In all compounds the attempt is made, by means of a thorough study of the conduct of the compounds, to trace out the connections existing between the constituent atoms. When this can be done for all the atoms contained in a molecule, the *structure* or *constitution* of the molecule of the compound is said to be determined. The structural formulas which have been determined by proper methods have proved of much value in dealing with chemical reactions, as they enable the chemist who *understands* the language in which they are written to see relations which might easily escape his attention without their aid. In order to *understand* them, however, the student must have a knowledge of

the reactions upon which they are based; and he is warned not to accept any chemical formula unless he can see the reasons for accepting it. He should ask the question, *Upon what facts is it based?* whenever a formula is presented for the first time. If he does this conscientiously, he will soon be able to use the language intelligently, and understand the relations that exist between the large number of compounds of carbon. If he does not, his mind will soon be in a hopeless muddle, and what he learns will be of little value. For the beginner, this advice is of vital importance: *Study with great care the reactions of compounds; study the methods of making them, and the decompositions which they undergo. The formulas are but the condensed expressions of the conclusions which are drawn from the reactions*

**General principle of classification of the compounds of carbon.** — The fundamental substances dealt with under the head of Inorganic Chemistry are, of course, the elements. The properties of the elements enable us to separate them, for study, into a number of groups; as, for example, the chlorine group, including bromine, iodine, and fluorine; the oxygen group, in which are included sulphur, selenium, and tellurium. To recall the method generally adopted, let us take the chlorine group. In studying the members of this group, there is found great similarity in their properties. Their hydrogen compounds next present themselves, and here also great similarity is met with. Then, in turn, the oxygen, and the oxygen and hydrogen compounds are taken up, and again the resemblances in properties between the corresponding compounds of chlorine, bromine, and iodine are observed. We thus have groups of elements, and of the compounds of these elements, as, —

Cl	ClH	ClO <sub>2</sub> H
Br	BrH	BrO <sub>2</sub> H
I	IH	IO <sub>2</sub> H, etc.

Of course, the chlorine group is quite distinct from the oxygen group and from all other groups; and each member of the chlorine group is, at least so far as we know, quite independent of the other members. We cannot make a bromine compound

from a chlorine compound, nor a chlorine compound from a bromine compound, without directly substituting the one element for the other.

Now, when we come to study the compounds of carbon, we shall find that the same general principle of classification is made use of; only, in consequence of the peculiarities of the compounds, the system can be carried out much more thoroughly; the members of the same group can be transformed one into the other, and it is also possible to pass from one group to another by means of comparatively simple reactions.

The simplest compounds of carbon are those which contain only hydrogen and carbon, or the *hydrocarbons*. All the other compounds may be regarded as derivatives of the hydrocarbons. To begin with, there are several groups or series of hydrocarbons, which correspond somewhat to the different groups of elements. The members of one and the same series of hydrocarbons resemble one another more closely than the members of one and the same series of elements. Although we have indications of the existence of more than ten series of these hydrocarbons, only three or four of the series are at all well known, and of these but two include more than two or three members that need to be treated of in this book.

Starting with any series of hydrocarbons, several classes of derivatives can be obtained by treating the fundamental compounds with different reagents. The chief classes of these derivatives are: (1) those containing halogens; (2) those containing oxygen, among which are the acids, alcohols, ethers, etc.; (3) those containing sulphur; and (4) those containing nitrogen. Corresponding to every hydrocarbon, then, we may expect to find representatives of these different classes of derivatives. But the relations existing between any hydrocarbon and its derivatives are the same as those existing between any other hydrocarbon and its derivatives. Hence, if we *know* what derivatives one hydrocarbon can yield, we know what derivatives we may expect to find in the case of every other hydrocarbon. The student who, for the first time, undertakes the study of the chemistry of the compounds of carbon is apt to

feel overwhelmed by the enormous number of them described in the book or by the lecturer. This large number is really not a serious matter. No one is expected to become acquainted with every compound. A great many of these need only be referred to for the purpose of indicating the extent to which the series to which they belong has been developed. In general, the members of any series so closely resemble one another, that, if we understand the simpler members, we have a fair knowledge of the more complicated members.

It is proposed, in this book, to treat only of the more important compounds and the more important reactions, the object being rather to give a clear, general view of the subject than detailed information regarding particular compounds. Should the student desire more specific information concerning the properties of any of the compounds mentioned, he can easily find it in some larger book. It will, however, hardly be profitable for him, at the outset, to burden his mind with details. He may thereby sacrifice the general view, which it is so important he should gain as quickly as possible.

The plan that will be followed is briefly this: Of the first series of hydrocarbons the first *two* members will be treated. Then the derivatives of these two will be taken up. These derivatives will serve admirably as representatives of the corresponding derivatives of other hydrocarbons of the same series, and of other series. Their characteristics and their relations to the hydrocarbons will be dwelt upon, as well as their relations to each other. Thus, by a comparatively close study of two hydrocarbons and their derivatives, a knowledge of the principal classes of the compounds of carbon may be acquired. After these typical derivatives have been discussed, the entire series of hydrocarbons will be taken up *briefly*, only such facts being dealt with at all fully as are not illustrated by the first two members.

After the first series has been studied in this way, and a clear idea of the relations between the various classes obtained, a second series will be taken up and treated in a similar way, and so on. But only a few of the series require much attention

at the beginning. The first series that will be used for the purpose of illustrating the general principles is one of the *two* most important series, and the only two that need be taken up at all fully at present. These are known as the *paraffin series* and the *benzene series*.

## CHAPTER II

### METHANE AND ETHANE — HOMOLOGOUS SERIES

If we were to study all the hydrocarbons known, and were then to arrange them in groups according to their properties, we should find that a large number of them resemble *marsh gas* in their general conduct. Some of the points of resemblance are these: They are very stable, resisting the action of most reagents; and nothing can be added to them directly, — if any change takes place in them, hydrogen is first given up. On arranging these substances according to the number of carbon atoms contained in them, we have a remarkable series, the first six members of which, together with their formulas, are included in the subjoined table: —

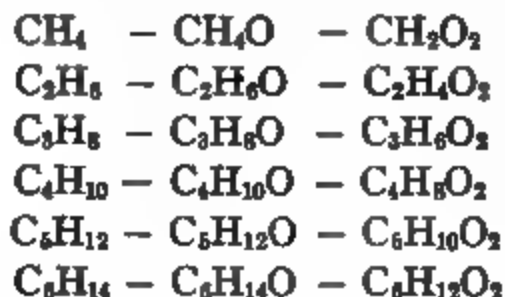
Methane (or Marsh Gas)	. . . . .	$\text{CH}_4$
Ethane	. . . . .	$\text{C}_2\text{H}_6$
Propane	. . . . .	$\text{C}_3\text{H}_8$
Butane	. . . . .	$\text{C}_4\text{H}_{10}$
Pentane	. . . . .	$\text{C}_5\text{H}_{12}$
Hexane	. . . . .	$\text{C}_6\text{H}_{14}$

On examining the formulas given, it will be seen that the difference in composition between any two consecutive members is represented by  $\text{CH}_2$ . Thus, adding  $\text{CH}_2$  to marsh gas,  $\text{CH}_4$ , we get ethane,  $\text{C}_2\text{H}_6$ ; adding  $\text{CH}_2$  to  $\text{C}_2\text{H}_6$ , we get  $\text{C}_3\text{H}_8$ , and so on, at each successive step. Any series of this kind, in which the successive members increase in complexity by  $\text{CH}_2$ , is called an *homologous series*.

Just as the members of an homologous series of hydrocarbons differ from one another by  $\text{CH}_2$ , or some multiple of it, so also the members of any class of derivatives of these hydrocarbons differ from one another in the same way, and form homologous series. Thus, running parallel to the hydrocarbons mentioned



above, there are two homologous series of oxygen derivatives, as indicated below:—



The relation observed between the members of the homologous series mentioned is by no means a peculiarity of the marsh gas series of hydrocarbons and of their derivatives, but is observed in the case of all other series of hydrocarbons and their derivatives.

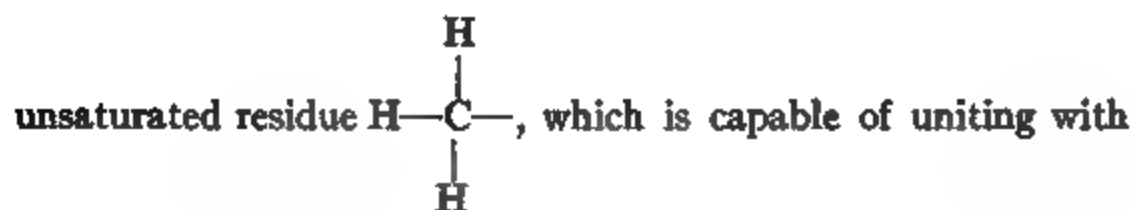
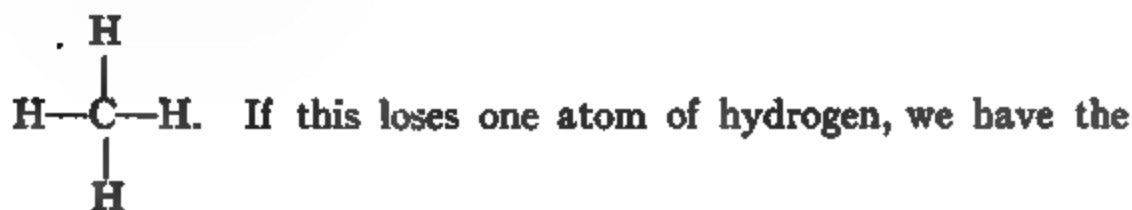
Strictly speaking, there is perhaps no analogy for this remarkable fact among the elements and their compounds, yet facts which suggest analogy are known. Take, for example, the chlorine series. We have

Chlorine,	with the atomic weight,	35.4.
Bromine,	"	80.
Iodine,	"	127.

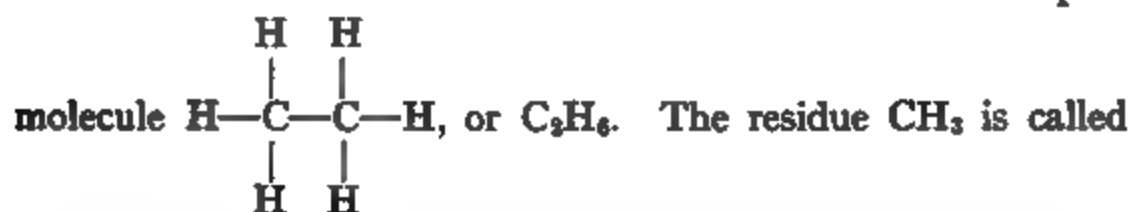
As is well known, the difference between the atomic weights of chlorine and bromine is approximately equal to the difference between those of bromine and iodine. In other words, there is a regular increase in the atomic weights of these similar elements, just as there is a regular increase in the molecular weights of the members of an homologous series. The explanation of homology in the sense in which the word is used in connection with the compounds of carbon is, as will be shown, very simple. A somewhat similar explanation of the relations between elements belonging to the same group has been put forward, but this necessitates a consideration of the structure of atoms, and it would lead too far to take that subject up here.

The view at present held in regard to the nature of homology is founded, primarily, upon the idea that carbon is quadrivalent.

If carbon is quadrivalent, it of course follows that the compound, marsh gas,  $\text{CH}_4$ , is saturated; that is, the molecule cannot take up anything without losing hydrogen. In order, therefore, that we may get a compound containing two atoms of carbon in the molecule, some of the hydrogen must first be given up. With our present views, we cannot conceive of combination taking place directly between the molecules  $\text{CH}_4$  and  $\text{CH}_4$ , but we can conceive of combination taking place between the residues  $\text{CH}_3$  and  $\text{CH}_3$ , to form a molecule  $\text{C}_2\text{H}_6$ , which in turn is saturated. Representing graphically what is believed to take place, we have, first, marsh gas, which we may represent thus,



another residue of the same kind to form the more complex



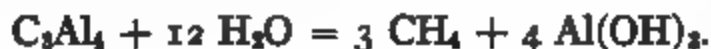
*methyl*. It appears therefore that the compound  $\text{C}_2\text{H}_6$ , ethane, is methylmethane or dimethyl, and the difference  $\text{CH}_2$  in composition between methane and ethane is thus accounted for. The evidence in favor of this view will be presented when the reactions by means of which the hydrocarbons are made are discussed. The explanation offered, and now accepted, involves the idea that carbon atoms unite with one another. And, as the explanation for the relation between the first and second member is, in principle, the same as for the relation between the second and third, the third and fourth, etc., it appears that this power

of carbon atoms to unite with one another is very extensive. *It is to the power that carbon possesses of forming homologous series, or to the power of the atoms of carbon to unite with one another, that we owe the large number of compounds of this element.*

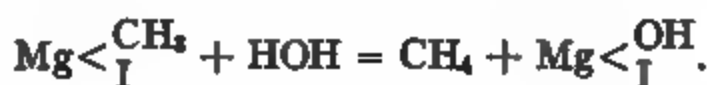
**Methane, marsh gas, fire damp,  $\text{CH}_4$ .** — This hydrocarbon is found rising from pools of stagnant water in marshy districts. If a bottle is filled with water and inverted with a funnel in its neck in such a pool, some of the gas can be collected by holding the funnel over the bubbles rising from the bottom. It is also found mixed with air, in coal mines, and sometimes issues from the earth, together with other gases, from petroleum wells. It is a constituent of natural gas.

It can be prepared

(1) By treating aluminium carbide,  $\text{C}_3\text{Al}_4$ , with water:—



(2) In pure condition by treating magnesium methyl iodide  $\text{H}_3\text{CMgI}$ , with water (112):—



(3) By passing hydrogen over a heated mixture of nickel and carbon.

(4) By reduction of carbon monoxide or dioxide with calcium hydride, or by heating finely divided carbon with calcium hydride.

(5) By direct combination of carbon and hydrogen at  $1200^\circ$ .

It is formed in the dry distillation of wood and coal, and is hence contained in coal gas. It is also formed, as its occurrence in marshes indicates, by the decomposition of organic matter under water. It is most readily made in the laboratory by heating a mixture of sodium acetate and soda-lime:—



It will be shown hereafter that many organic acids break down in a similar way, yielding a hydrocarbon and a carbonate.

*Properties.* Marsh gas is colorless and has a pleasant alli-<sup>garlic</sup>aceous odor. It is slightly soluble in water, but not so much so as to prevent its collection over water. It burns. Its mixture with air often explodes when a flame is applied. This mixture is the cause of some of the explosions in coal mines. In mines it is known as fire damp. The explosion is due to the rapid combustion of the marsh gas. The products are carbon dioxide and water: —



Carbon dioxide is known to the miner as choke damp or after damp.

The most common cause of explosions in coal mines is coal dust. The explosion is, in fact, an extremely rapid combustion of the carbon, giving carbon monoxide and dioxide.

Reagents, in general, do not act readily upon marsh gas. Chlorine in sunlight gradually takes the place of the hydrogen, forming substitution products which will be treated of under the head of the halogen derivatives of methane. The simplest of them has the composition represented by the formula  $\text{CH}_3\text{Cl}$ , and is known as *chloromethane* or *methyl chloride* (26).

**Ethane, dimethyl,  $\text{C}_2\text{H}_6$ .** — Ethane rises from the earth from some of the gas wells in the regions in which petroleum occurs. It is also found dissolved in crude petroleum.

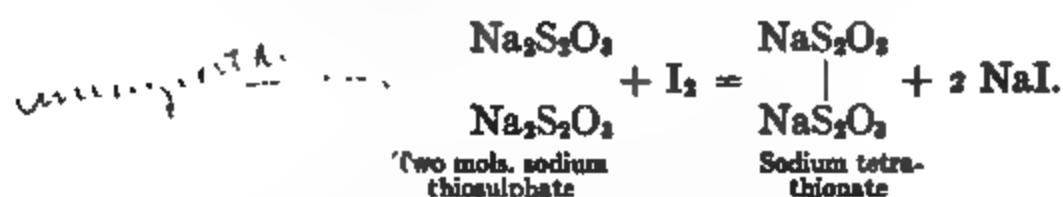
It can be made from methane by introducing a halogen and making a compound like chloromethane,  $\text{CH}_3\text{Cl}$ . As the corresponding iodine derivative is less volatile, it is used. This iodomethane,  $\text{CH}_3\text{I}$ , is treated with zinc or sodium in some neutral medium, as, for example, anhydrous ether. The reaction which takes place is represented thus:—



Hence the name dimethyl.

This method of building up more complex from simpler hydrocarbons has been used extensively; and it is well adapted to show the relations between the substances formed and the simpler ones from which they are made.

An operation of the kind involved in the above mentioned preparation of ethane is called a *synthesis*. The essential feature of the synthesis is the formation of a more complex substance from simpler ones. Our knowledge of the structure of the compounds of carbon is largely dependent upon the use of various methods of synthesis. For example, in the case under consideration, the synthesis gives us at once a clear view of the relations between ethane and methane, and also suggests that homology may be due to similar relations between the successive members of the series, — a view which is fully confirmed by the synthetical preparation of the higher members. A similar method of synthesis has been used in the preparation of sodium tetrathionate from sodium thiosulphate. The action is represented thus: —



**Properties.** Ethane is a colorless, tasteless gas with an agreeable ethereal odor. It resembles methane very closely in its chemical and physical properties. It is made on the large scale by the reduction of ethylene.  $\text{C}_2\text{H}_4$

## CHAPTER III

### HALOGEN DERIVATIVES OF METHANE AND ETHANE

**Substitution.** — When methane and chlorine are brought together in sunlight, hydrochloric acid gas is given off, and one or more compounds are obtained, according to the length of time the action continues.

The simplest product thus obtained has the composition  $\text{CH}_3\text{Cl}$ . The reaction is represented by the equation: —



The result is the substitution of one atom of chlorine for one atom of hydrogen. This is known as *substitution*. The action may proceed further and result in the formation of a second product thus: —

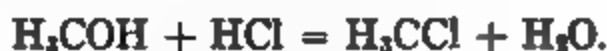


While these reactions illustrate the phenomenon of substitution in its simplest form, the substitution products of methane and ethane are more readily made by other methods.

We shall find that most hydrocarbons react with the halogens and some with other reagents, such as nitric acid, sulphuric acid, and that thus a large number of derivatives can be made, differing from the hydrocarbons in that they contain one or more halogen atoms or complex groups in the place of the same number of hydrogen atoms. It must be borne in mind that the mere fact that chlorine, in acting upon marsh gas, is substituted for an equivalent quantity of hydrogen, does not prove that the chlorine in the product occupies the same place that the replaced hydrogen did. Nevertheless, a careful study of all the facts regarding the products thus formed has led to the belief that the substituting atom or residue does occupy the same place, or bear the same relation to the carbon atom that the hydrogen did.

The name *substitution products* properly includes all products made from the hydrocarbons, or from other carbon compounds, by the substitution process. The principal ones are those formed by the action of the halogens, or the *halogen substitution products*; those formed by the action of nitric acid, or the *nitro substitution products*; and those formed by the action of sulphuric acid, or the *sulphonic acids*.

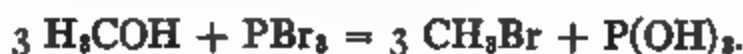
**Chloromethane, methyl chloride,  $\text{CH}_3\text{Cl}$ .** — Chloromethane can be made by chlorinating methane (26) or by the action of hydrochloric acid on methyl alcohol: —



For this reason it is called methyl chloride. It will be shown that methyl alcohol is methyl hydroxide, and that it acts towards acids like a metallic hydroxide.

It is a colorless gas having an ethereal odor. It burns with a white flame bordered with green. Boiling point  $-23.73^\circ$ ; soluble in water and alcohol. Used in local anæsthesia and as a methylating agent.

**Bromomethane, methyl bromide,  $\text{CH}_3\text{Br}$ .** — This is made from methyl alcohol by the action of hydrobromic acid or by treating the alcohol with phosphorus and bromine: —

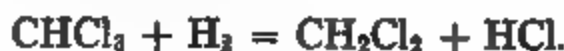


It does not burn. It is a gas readily condensed to a liquid. Boiling point  $4.5^\circ$ .

**Iodomethane, methyl iodide,  $\text{CH}_3\text{I}$ ,** is made by the action of hydriodic acid on methyl alcohol or by treating methyl alcohol with phosphorus and iodine.

It is a colorless liquid, boiling at  $45^\circ$ .

**Dichloromethane, methylene chloride,  $\text{CH}_2\text{Cl}_2$ .** — Methylene chloride is made from chloroform in alcoholic solution by the action of zinc and hydrochloric acid: —



It can also be made by the action of chlorine on methylene iodide: —



It is a by-product of the manufacture of chloroform from carbon tetrachloride. It boils at  $41.6^{\circ}$  and is used as a solvent in place of chloroform. Specific gravity, 1.432.

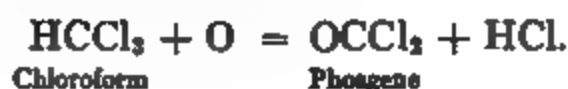
**Dibromomethane, methylene bromide,  $\text{CH}_2\text{Br}_2$ .** — Methylene bromide is made by the action of bromine on methylene iodide. It boils at  $96.5^{\circ}$ – $97.5^{\circ}$ . It can also be made from bromoform by reverse substitution.

**Diiodomethane, methylene iodide,  $\text{CH}_2\text{I}_2$ .** — Methylene iodide boils at  $181^{\circ}$  with partial decomposition. It is the heaviest of all known organic liquids. Specific gravity, 3.33 at  $18^{\circ}$ . It is made from iodoform, triiodomethane,  $\text{CHI}_3$ , by reducing it with hydriodic acid and phosphorus: —



The phosphorus combines with the iodine set free in the reaction. This is a case of *reverse substitution*, hydrogen being substituted for iodine.

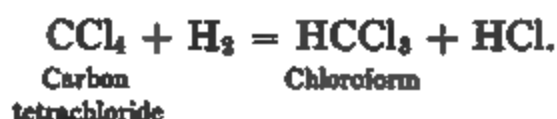
**Chloroform,  $\text{CHCl}_3$ .** — Chloroform was first used as an anæsthetic in surgical operations by Dr. Simpson of Edinburgh in 1848. It decomposes into phosgene and hydrochloric acid in the presence of light and air: —



This decomposition is said to be prevented by the presence of a small amount of alcohol, so that the chloroform of commerce always contains from 0.6 to 1 per cent of alcohol. It is not much used as an anæsthetic at the present time in this country; ether or a mixture of nitrous oxide gas, oxygen and ether has taken its place, as they are much safer than chloroform. Chloroform is made in the laboratory from alcohol or acetone, water, and bleaching powder. The reactions will be explained under chloral and acetone. It has an ethereal odor and a sweet taste. It is a heavy liquid, specific gravity 1.5, and is somewhat soluble in water (7 grams in a liter). It boils at  $61.2^{\circ}$  and solidifies at  $-63.2^{\circ}$ . Chloroform is an excellent solvent for many organic compounds, and it is largely used for this purpose



and for cleaning fabrics. It does not burn. It is a powerful antiseptic, preventing fermentation and putrefaction. Chloroform is now made on the large scale from carbon tetrachloride by reverse substitution, iron and water being used to furnish the nascent hydrogen:—



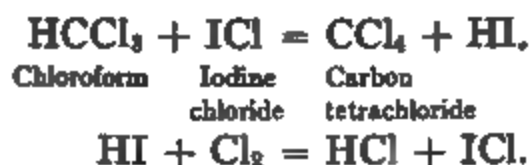
The nascent hydrogen also acts on some of the chloroform to give methylene chloride, which is a by-product of this method:—



**Bromoform,  $\text{CHBr}_3$ .**—Bromoform is made from alcohol or acetone by the action of bromine and an alkali. Boiling point  $146^\circ$ . It is used as a remedy in whooping cough. The bromoform of the U. S. Pharmacopeia contains 4 per cent by weight of absolute alcohol.

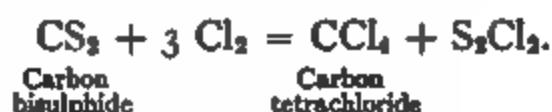
**Iodoform,  $\text{CHI}_3$ .**—Iodoform is used extensively in surgery as it prevents infection, and aids in the healing of wounds. It is, however, not used as much as formerly. It is made from alcohol or acetone by the action of iodine in the presence of an alkali. It is volatile with steam and evaporates even at ordinary temperatures. It crystallizes in yellow, hexagonal plates that melt at  $119^\circ$ . It has a penetrating, sweetish odor which is noticed in hospitals where it is used. It is an unstable substance and decomposes readily, yielding iodine as one of its products. It is to this fact that it owes its antiseptic property.

**Carbon tetrachloride,  $\text{CCl}_4$ .**—Carbon tetrachloride cannot be made by the action of chlorine on carbon, although fluorine acts readily on carbon to form carbon tetrafluoride. It can be made by the action of chlorine on chloroform in the presence of iodine:—



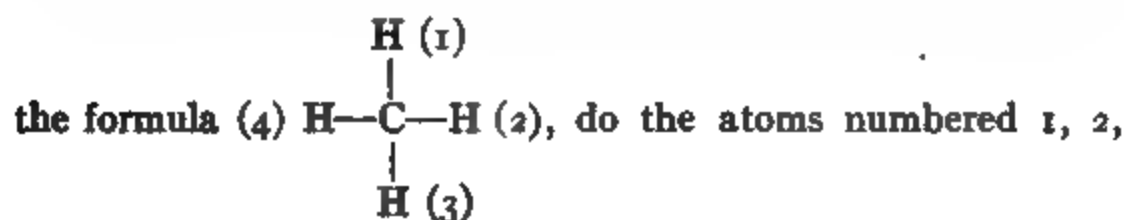
The iodine serves as a *chlorine carrier*. It first combines with the chlorine to form iodine chloride. This then reacts with the chloroform, giving carbon tetrachloride and hydriodic acid. The hydriodic acid is immediately acted upon by the chlorine to form hydrochloric acid and regenerate iodine chloride. Thus it will be seen that the iodine acts as a chlorine carrier and, as it is used over and over again, only a very small amount of it need be present. These chlorine carriers are much used in chlorinating organic compounds and are sometimes indispensable. Thus chlorine acts very slowly on chloroform, but in the presence of iodine the reaction takes place readily.

Carbon tetrachloride is made on the large scale by the action of chlorine on carbon bisulphide in the presence of a chlorine carrier:—



The action consists in the substitution of chlorine for sulphur. The carbon bisulphide is made by the action of sulphur vapor on red-hot carbon. Carbon tetrachloride is a colorless liquid, having an odor similar to that of chloroform and boiling at  $76.74^\circ$ . It is an excellent solvent, especially for fats, rubber, etc., and, as it is non-inflammable, it is much used for the extraction of fats and the removal of grease spots. It is also used as a fire-extinguisher under the name of *Pyrene*. As stated above, chloroform is now made from it on the large scale by reverse substitution.

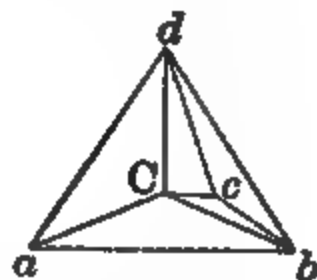
**Equivalence of the hydrogen atoms in methane.**—The interesting question suggests itself whether the hydrogen atoms in methane all bear the same relation to the carbon atom. Assuming that the carbon atom is quadrivalent, and that each of the four hydrogen atoms is in combination with it, as indicated in



3, and 4 bear the same relation to the carbon or not? If they do not, then, on replacing H (1) by chlorine, the product should be different from that obtained by replacing H (2), H (3), or H (4); or, it should be possible to make more than one variety of chloromethane and of similar products. This subject is an extremely difficult one to deal with. It can only be said that, although chloromethane has been made in several ways, the product obtained is always the same one; and the same is true of all other monosubstitution products of methane. *So far as evidence of this kind goes, we have no reason for believing that there are any differences between the hydrogen atoms of methane.*

This conclusion is of fundamental importance in dealing with the higher members of the methane series, and, indeed, in dealing with all carbon compounds.

The formula on page 29 represents the carbon atom and the four hydrogen atoms in a plane. As will be pointed out later, however, there is experimental evidence showing that the hydrogen atoms are in fact arranged *symmetrically in space* around the carbon atom. This important conception is represented by the adjoining figure.



The carbon atom is represented as situated at the centre of a regular tetrahedron and the four hydrogen atoms at the solid angles of the tetrahedron, *a*, *b*, *c*, and *d*. Thus each hydrogen atom bears the same relation to the carbon atom. —4

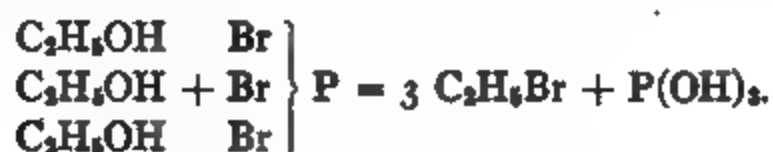
Chloroethane, ethyl chloride,  $C_2H_5Cl$ .

Bromoethane, ethyl bromide,  $C_2H_5Br$ .

Iodoethane, ethyl iodide,  $C_2H_5I$ . A'

These substances are all liquids having pleasant ethereal odors. The first boils at  $12.5^\circ$ , the second at  $38.37^\circ$ , and the third at  $72^\circ$ . They are most readily made from alcohol, by treating it with the corresponding halogen acids. The bromide and iodide can also be made by treating the alcohol with red phosphorus and the halogen. The action is similar to that involved in making hydrobromic acid by treating water with

red phosphorus and bromine. It will be shown that alcohol is a hydroxide in which hydroxyl, OH, is in combination with the group  $C_2H_5$ , called *ethyl*, as represented in the formula  $C_2H_5OH$ . When bromine is brought in contact with red phosphorus, the tribromide,  $PBr_3$ , is formed, and this acts upon the alcohol thus: —



When water is used instead of alcohol, the bromine appears in combination with hydrogen as hydrobromic acid: —



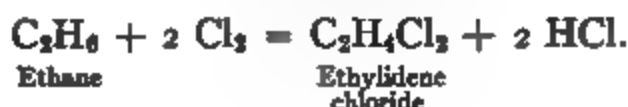
Ethyl chloride and ethylidene chloride,  $C_2H_4Cl_2$ , are by-products of the manufacture of chloral. Ethyl bromide is made on the large scale and is used in making diethylaniline and other ethyl derivatives.

Among the many halogen substitution products of ethane containing more than one halogen atom, two are of special interest. These are the two *dichloroethanes*, both of which are represented by the formula  $C_2H_4Cl_2$ . The existence of these substances, having the same composition but different properties, affords a good example of *isomerism*.

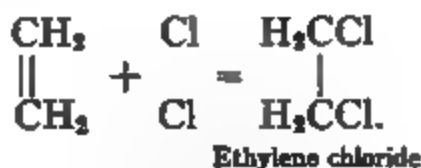
**Isomerism.** — One of the most striking and interesting facts with which we become familiar in studying carbon compounds is the frequent occurrence of two, and often more, compounds containing the same elements in the same proportions by weight. Substances which bear this relation to one another are said to be *isomeric*.

*Isomerism* is of two kinds: (1) Compounds may have the same percentage composition and the same molecular weight. Such compounds are said to be *metameric*. The dichloroethanes,  $C_2H_4Cl_2$ , for example, are metameric. (2) Compounds that have the same percentage composition but different molecular weights are said to be *polymeric*. Benzene,  $C_6H_6$ , and styrene,  $C_8H_8$ , are polymers of acetylene,  $C_2H_2$ .

The cause of isomerism is undoubtedly to be found in the different ways in which the atoms of isomeric compounds are linked together. Our structural formulas, which show the relations between the parts of compounds that have been traced out by a study of the chemical conduct of these compounds, give us an insight into the cause of isomerism. To illustrate, take the two dichloroethanes. One of these is made by treating ethane, the other by treating ethylene,  $C_2H_4$ , with chlorine. In the first case the action is substitution.



In the second, the chlorine is added directly to ethylene, thus:—



The product from ethylene is called *ethylene chloride*, boiling point  $83.5^\circ$ ; that from ethane, *ethylidene chloride*, boiling point  $59.2^\circ$ . It will be shown that ethylene is represented by the for-

mula  $\begin{array}{c} CH_2 \\ || \\ CH_2 \end{array}$ ; that is, it is unsaturated. In it only two hydrogen

atoms are in combination with each of the carbon atoms. Now, if chlorine is brought in contact with this substance, we should naturally expect each of the carbon atoms to take up one atom of chlorine, and thus to become saturated, as represented in the above equation.

Chlorine is taken up, and it is believed that the ethylene chloride obtained has the structure represented by the above formula, the distinctive feature of which is that each of the chlorine atoms is in combination with a different carbon atom.

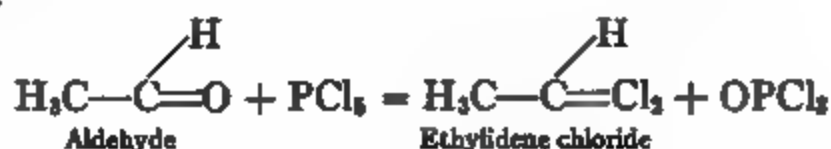
We can, however, conceive of another possibility; viz., both the chlorine atoms may be in combination with the same carbon

atom, as represented in the formula  $\begin{array}{c} HCCl_2 \\ | \\ CH_2 \end{array}$ , and we should be

inclined to the view that this represents the structure of ethylidene chloride, as there are but *two* dichloroethanes known and possible according to theory. Fortunately there is experimental evidence to support this view. It will be shown that aldehyde

has the formula  $\begin{array}{c} \text{O}=\text{CH} \\ | \\ \text{CH}_3 \end{array}$ . When aldehyde is treated with phos-

phorus pentachloride, two chlorine atoms take the place of the oxygen:—



A product that must be represented by the above formula is formed, and this is identical with ethylidene chloride made from ethane. Thus it will be seen that the difference between the two isomeric compounds, ethylene chloride and ethylidene chloride, is due to the fact that in the former the two chlorine atoms are in combination with different carbon atoms, while in the latter both chlorine atoms are in combination with the same carbon atom.

Hexachloroethane,  $\text{C}_2\text{Cl}_6$ , a solid, is a by-product of the manufacture of chloroform:—

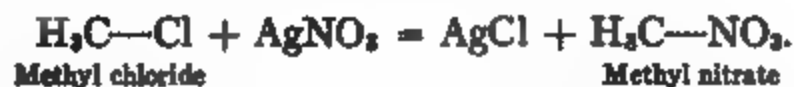


Its odor suggests that of camphor.

This formation of hexachloroethane is analogous to the synthesis of ethane from methyl iodide and sodium (23).

*General characteristics of the halogen derivatives of methane and ethane.* The one characteristic to which it is desirable that special attention should be called is the condition of the halogens in these compounds. In general, chlorine in combination in inorganic compounds can be detected by means of a solution of silver nitrate, for when dissolved in water these compounds are ionized. The halogen substitution products of the hydrocarbons are not ionized by water, and the chlorine in them cannot be detected by means of silver nitrate in the ordinary way. On the other hand, when chloromethane is

heated with silver nitrate in a sealed tube, the chlorine is replaced:—



Sodium and zinc have the power of extracting the chlorine, bromine, etc., from halogen derivatives, and this fact is taken advantage of in the synthesis of many hydrocarbons (23).

All halogen derivatives are reduced to the hydrocarbon from which they are derived by the action of nascent hydrogen:—



## CHAPTER IV

### OXYGEN DERIVATIVES OF METHANE AND ETHANE

THERE are several classes of oxygen derivatives of the hydrocarbons. Among them are the important compounds known as alcohols, ethers, aldehydes, and acids. Each of these classes will be taken up in turn.

#### 1. ALCOHOLS

Among the most important oxygen derivatives are the alcohols, of which methyl alcohol and ethyl alcohol are the best-known examples. As far as composition is concerned, these compounds bear simple relations to the two hydrocarbons, methane and ethane. These relations are indicated by the formulas:—



The molecule of the alcohol differs from that of the corresponding hydrocarbon by one atom of oxygen. In order to understand the chemical nature of alcohols, it will be best to study with some care the reactions of one; and we may take for this purpose the simplest one of the series, methyl alcohol.

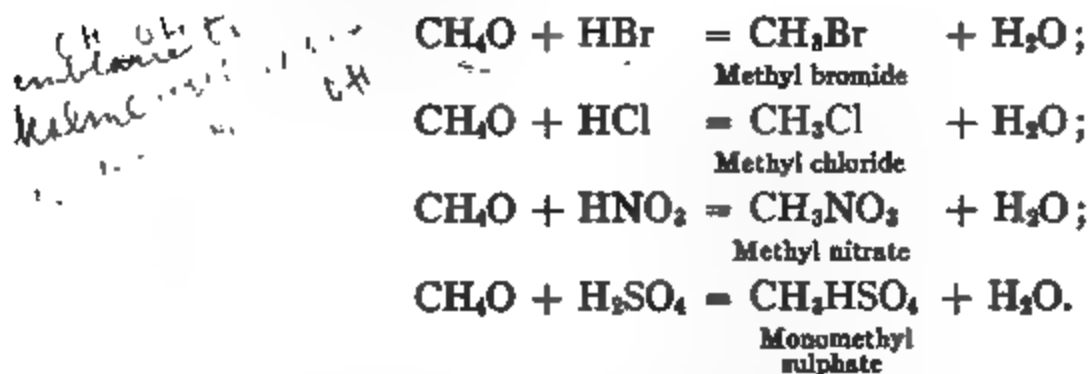
**Methyl alcohol, carbinol, methanol,  $\text{CH}_4\text{O}$ .**— This alcohol is also known as wood alcohol or wood spirit. It is found in nature in combination with salicylic acid in the oil of winter-green. It is formed, together with many other substances, in the dry distillation of wood. When wood is distilled for the purpose of making charcoal an aqueous distillate is obtained containing methyl alcohol, acetic acid, and acetone. This is the source of methyl alcohol and the chief source of acetic acid



and acetone. The acetic acid is neutralized by means of milk of lime and the methyl alcohol and acetone are distilled off from the aqueous solution and separated by fractional distillation. It is difficult to eliminate all the acetone by fractional distillation alone, so that the methyl alcohol of commerce generally contains some acetone, though in recent years the apparatus used for fractional distillation has been so improved that methyl alcohol practically free from acetone is thus obtained.

Methyl alcohol is a liquid that boils at  $64.7^{\circ}$ , melts at  $-97.8^{\circ}$ , and has the specific gravity 0.81 at  $0^{\circ}$ . It closely resembles ordinary alcohol in all its properties. It burns with a non-luminous flame. When taken into the system it intoxicates. It is poisonous. Blindness and death may be caused by its internal use. It is an excellent solvent for fats, oils, resins, and other organic substances, and is extensively used for this purpose, and for methylating and the preparation of formaldehyde and in denaturing alcohol.

1. *Action of hydrochloric, hydrobromic, and other acids on methyl alcohol.* The action of a few acids is represented by the following equations:—

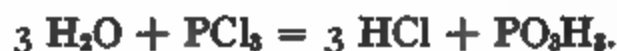


The action is plainly suggestive of that of alkaline hydroxides or bases. In each case the acid is either wholly or partly neutralized and water is formed, just as the acid would be neutralized by potassium hydroxide.

2. *Action of phosphorus trichloride.* When phosphorus trichloride acts on methyl alcohol, the products are chloromethane and phosphorous acid:—



Here one atom of chlorine is substituted for an atom of hydrogen<sup>24311 1'</sup> and an atom of oxygen, the reaction being like that which<sup>44211</sup> takes place between water and phosphorus trichloride: —



This fact would lead us to suspect that there is a close resemblance between the alcohol and water. <sup>24311 1'</sup>

3. *Action of potassium and sodium.* When potassium is brought in contact with pure methyl alcohol, hydrogen is given off, and a compound containing potassium is formed: —



Further treatment of this compound with potassium causes no further evolution of hydrogen, so that plainly one of the four hydrogen atoms contained in methyl alcohol differs from the other three.

The resemblance between methyl alcohol and the alkaline hydroxides; the substitution of chlorine for hydrogen and oxygen; the resemblance between the alcohol and water; and, finally, the substitution of potassium for one, and only one, hydrogen atom, lead to the conclusion that the alcohol contains hydrogen and oxygen in combination, and that the characteristic reactions are due to the presence of the group called *hydroxyl*, OH. The analogy between the alcohol, an alkaline hydroxide, and water is shown by these formulas: alcohol,  $\text{H}_3\text{COH}$ ; hydroxide,  $\text{KOH}$ ; water,  $\text{HOH}$ . Thus water appears as the type of both the hydroxide and the alcohol, and they may be regarded as derived from water by substituting the methyl group,  $\text{CH}_3$ , for one hydrogen atom in the case of the alcohol, and substituting an atom of the metal potassium for one hydrogen atom in the case of the hydroxide. Thus methyl alcohol is methyl hydroxide. Or, on the other hand, methyl alcohol may be regarded as marsh gas in which one of the hydrogen atoms is replaced by hydroxyl. The two views are in fact identical.

To test the correctness of this view, we may make methyl alcohol in some way that will show us of what parts it is made

up. Thus, we may start with marsh gas, and introduce a halogen, as bromine:—



Now, when bromomethane and silver hydroxide are brought together, reaction takes place as represented in the equation:—



and methyl alcohol is formed. This furnishes strong evidence in favor of the view expressed in the formula  $\text{CH}_3\text{OH}$ .

The reactions above presented show that the part of methyl alcohol that corresponds to the metal in the hydroxide is the group  $\text{CH}_3$ . This it is which enters into the acids in place of their hydrogen, and this remains unchanged when potassium acts upon the alcohol. It has received the name *methyl*. Hence we have the names methyl alcohol, methyl bromide, methyl ether, etc. A group which, like methyl, appears in a number of compounds is called a *radical*, or *residue*. These names are intended simply to designate that part of a carbon compound which remains unchanged when the compound is subjected to various transforming influences.

The two most characteristic reactions of methyl alcohol are: (1) its power to form salt-like compounds when treated with strong acids; and (2) its power to form an acid containing the same number of carbon atoms when oxidized.

The neutral compounds formed with strong acids correspond to the salts of the metals, only they contain the radical, methyl,  $\text{CH}_3$ , in place of the metals. They are called *ethereal salts* or *esters*.

The acid formed by oxidation of methyl alcohol has the composition expressed by the formula  $\text{CH}_2\text{O}_2$ , and is known as *formic acid*. It contains one atom of oxygen more and two atoms of hydrogen less than the alcohol from which it is formed. It will be shown that this acid is the first member of an important series of acids, known as the *fatty acids*, each of which bears the same relation to a hydrocarbon containing the same number of carbon atoms that formic acid bears to marsh gas,

**Ethyl alcohol, methyl carbinol, ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ .** — Ethyl alcohol occurs in a number of plants in the free condition and in the form of ethyl esters of organic acids. It also occurs in small quantity in rain and snow and in the atmosphere. Fresh bread made with yeast contains a small quantity of alcohol.

This is the best-known substance belonging to the class of alcohols. It is known also by the names *spirit of wine*, *ordinary alcohol*, and *grain alcohol*.

The one method of manufacture upon which we are dependent for alcohol is the fermentation of sugar solutions.

**Fermentation.** — Whenever a plant juice containing sugar is left exposed to the air, it gradually undergoes a change by which it loses its sweet taste. Usually the change consists in a breaking down of the sugar into carbon dioxide and alcohol. The equation:—



expresses what takes place in the process which is known as *alcoholic fermentation*. Ninety-five per cent of the sugar can be converted into alcohol and carbon dioxide. It has been shown that fermentation is caused by the presence of microorganisms, either animal or vegetable. These organisms, which are known as *ferments*, are of different kinds, and cause different kinds of fermentation with different products. Among them the following may be specially mentioned:—

1. *Alcoholic or vinous fermentation.* This is caused by a vegetable ferment, *saccharomyces* or *yeast*. The ferment consists of small, round cells arranged in chains. The products of its action are alcohol and carbon dioxide.

2. *Lactic acid fermentation.* This is due to a vegetable ferment, *bacterium lactis*, which is contained in sour milk. It has the power of transforming sugar into lactic acid.

3. *Acetic acid fermentation.* This is due to a peculiar vegetable ferment, *bacterium aceti*, which oxidizes alcohol in the presence of air to acetic acid. The chemical changes brought about

by these organisms are due to the action of *enzymes*,<sup>1</sup> which are produced by the organisms. The enzyme that decomposes sugar into alcohol and carbon dioxide is called *zymase*.

The germs of various ferments are in the air; and, whenever they find favorable conditions, they develop and produce their characteristic effects. They will not develop in a solution of pure sugar. The sugar from which alcohol is obtained is not ordinary cane sugar, but *grape sugar*, or *glucose*, and *fructose*. In order that the ferment may grow, there must be present in the solution, besides the sugar, substances which contain nitrogen and inorganic salts, especially phosphates and potassium salts. These, as well as the sugar, are contained in the juices pressed out from fruits, and hence these juices readily undergo fermentation.

In the manufacture of alcohol a solution containing sugar is first prepared from sugar beets or molasses or from some kind of grain or potatoes. In case the solution contains grape sugar or fruit sugar, this undergoes fermentation directly when the yeast is added. If the substance in solution is cane sugar, this is first changed by the enzyme, *invertase*, present in the yeast into grape sugar and fruit sugar, and the fermentation then takes place as in the first case. When grain (Indian corn in this country) or potatoes are used, the starch is first converted into sugar by the enzyme, *diastase*, of the malt.

To obtain alcohol from fermented liquids, these must be distilled. The alcohol thus obtained contains water and a mixture of other alcohols called *fusel oil*. The latter can be removed partly by fractional distillation, and the last portions can be got rid of by filtering through charcoal. The water cannot be removed completely by fractional distillation, though a product containing 95-96 per cent of alcohol can be obtained in this way. This mixture has a constant boiling point (78.15°).

*Absolute alcohol* is ordinary alcohol from which the water has been removed by means of some dehydrating agent, as quicklime, barium oxide, or benzene. By continued treatment with freshly burned lime the quantity of water can be reduced to

<sup>1</sup> *The Nature of Enzyme Action*: W. M. Bayliss, 4th ed.

less than one-half per cent, and this small quantity can be removed by treatment with metallic sodium or calcium.

On the large scale the dehydrating agent used is benzene. The ternary mixture (water, alcohol, and benzene) boils at  $64.85^{\circ}$  and comes over first. If there is more than sufficient benzene to carry over *all* the water, and if the alcohol is present in excess, the ternary mixture will be followed by the binary mixture (alcohol and benzene, b. p.  $68.25^{\circ}$ ) and the last substance to come over will be absolute alcohol (b. p.  $78.3^{\circ}$ ) free from water and benzene.<sup>1</sup>

Ethyl alcohol has a spirituous, pleasant odor. It is claimed, however, that absolutely pure anhydrous alcohol has no odor. It remains liquid at low temperatures, but it has been converted into a solid which melts at  $-117.3^{\circ}$ . It boils at  $78.37^{\circ}$  at 760<sup>mm</sup>. Like methyl alcohol it burns with a non-luminous flame, which does not leave a deposit of soot on substances placed in it. It is very hygroscopic. When mixed with air, its vapor explodes when a flame is applied. Its effects upon the human system are well known. It intoxicates when taken in dilute form, while in concentrated form it is poisonous. When taken internally in large doses, it lowers the temperature of the body from  $0.5^{\circ}$  to  $2^{\circ}$ , although the sensation of warmth is experienced.

**Denatured alcohol.** — Alcohol to which something has been added to make it unfit for use as a beverage can be withdrawn from bond for use in the industries without payment of the internal revenue tax on alcohol. Such alcohol is called *denatured alcohol*. Various substances are employed as denaturing agents. Among those authorized by the United States government are methyl alcohol, benzine, and pyridine bases. Completely denatured alcohol contains methyl alcohol and benzine or methyl alcohol and pyridine bases. This is used as a source of heat, in gas engines in place of gasoline, and as a solvent in the purification and preparation of a large number of pharmaceutical products, dyestuffs, etc., and in the preparation of collodion, celluloid, and smokeless powders.

<sup>1</sup> See *Distillation: Processes and Principles*, by Sidney Young.

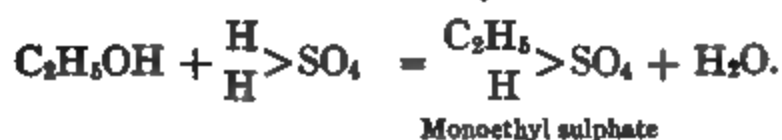
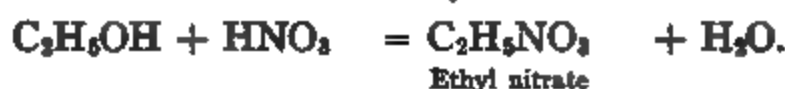
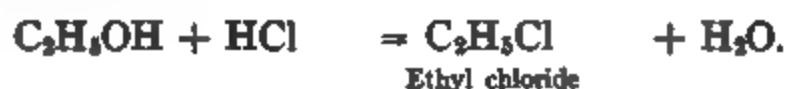
**Alcohol for scientific work.** — Educational institutions have the privilege of withdrawing ethyl alcohol from bond for use in scientific work and in teaching, without the payment of the tax.

**Alcoholic beverages.** — Most of the alcohol manufactured at the present time is used (except in the United States) in the form of beverages.

The milder forms of beer contain from 2 to 3 per cent; light wines, such as claret, about 8 per cent; while whisky, brandy, rum, and other distilled liquors sometimes contain as much as 60 to 75 per cent. These distilled liquors are ordinary alcohol with water and small quantities of substances obtained from the fruit or grain used in their preparation, or obtained by standing in barrels made of oak wood. The flavors of the beverages are due to these substances.

**Chemical conduct of ethyl alcohol.** Ethyl alcohol conducts itself chemically like methyl alcohol. The products formed contain the radical, ethyl,  $C_2H_5$ , instead of methyl.

**Reactions of ethyl alcohol.** With acids it forms ethereal salts or esters: —

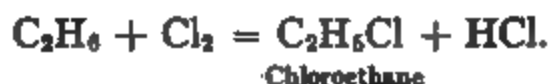


With phosphorus trichloride the hydroxyl group is replaced by chlorine: —

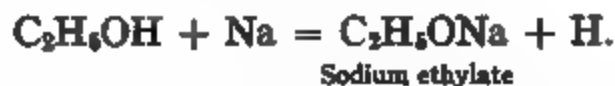


A similar reaction takes place with phosphorus tribromide and with phosphorus and iodine, giving ethyl bromide and ethyl iodide.

The ethyl chloride formed in the reactions above represented is identical with the chloroethane formed by the action of chlorine on ethane: —

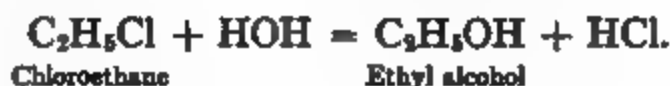


Potassium and sodium react readily with the alcohol in the cold, forming ethylates:—



As in the case of methyl alcohol only one atom of hydrogen is replaced by the metal—the one combined with the oxygen.

Finally, alcohol can be made synthetically from ethane by first making chloroethane and then heating with water:—



All these reactions indicate that ethyl alcohol is made up of the radical ethyl,  $\text{C}_2\text{H}_5$ , joined to hydroxyl,  $\text{OH}$ , or that it is ethane in which one hydrogen atom is replaced by a hydroxyl

group. Its structural formula is therefore  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{COH} \end{array}$ . It will be seen

that it is methyl alcohol in which a methyl group,  $\text{CH}_3$ , is substituted for a hydrogen atom of the original methyl group. It is hence called methyl carbinol.

When oxidized, ethyl alcohol gives acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ . This is the reason why cider or wine changes to vinegar when exposed to the air. Methyl and ethyl and other radicals of the marsh gas series are called *alkyl* groups.

## 2. ETHERS

When an alcohol is treated with potassium or sodium, compounds are formed having the formulas  $\text{CH}_3\text{ONa}$ ,  $\text{CH}_3\text{OK}$ ,  $\text{C}_2\text{H}_5\text{OK}$ ,  $\text{C}_2\text{H}_5\text{ONa}$ . If sodium methylate,  $\text{CH}_3\text{ONa}$ , is treated with a monohalogen derivative of a hydrocarbon, as, for example, iodomethane,  $\text{CH}_3\text{I}$ , reaction takes place thus:—



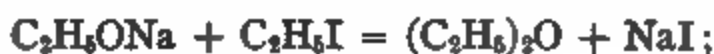
This reaction shows that the product must be represented by the formula  $\text{H}_3\text{C—O—CH}_3$ , or  $(\text{CH}_3)_2\text{O}$ . It is dimethyl oxide and is isomeric with ethyl alcohol. Comparing it with methyl alcohol, it will be seen that it is obtained from the alcohol



by replacing the hydrogen of the hydroxyl by methyl,  $\text{CH}_3$ . Just as the alcohol is analogous to the hydroxide,  $\text{KOH}$ , so the dimethyl oxide is analogous to the oxide,  $\text{K}_2\text{O}$ . It is the first representative of a class of compounds known as *ethers*, which are analogous to the oxides of the univalent metals.

**Dimethyl ether**,  $\text{C}_2\text{H}_6\text{O}$ ,  $(\text{CH}_3)_2\text{O}$ , is a gas readily condensed to a liquid, boiling at  $-23.6^\circ$ , freezing point  $-138.5^\circ$ . It acts as an anæsthetic. One volume sulphuric acid absorbs 600 volumes dimethyl ether. This ether is made by the action of sulphuric acid on methyl alcohol. It is more soluble in water than ethyl ether. It is obtained on the large scale as a by-product of the manufacture of dimethylaniline (348).

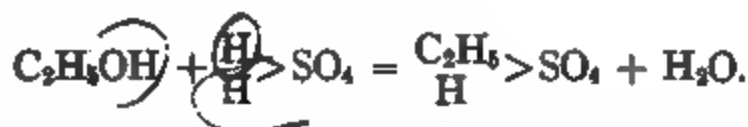
**Ethyl ether**,  $\text{C}_4\text{H}_{10}\text{O}$ ,  $(\text{C}_2\text{H}_5)_2\text{O}$ . — This is the substance commonly known as *ether*, or *sulphuric ether*. The latter name is given to it because sulphuric acid is used in its manufacture. It is the most important representative of the class, and has been known since the first half of the sixteenth century. Ether can be made from alcohol by making the sodium derivative of alcohol,  $\text{C}_2\text{H}_5\text{ONa}$ , and heating this with iodoethane thus:—



or by converting the alcohol into ethyl iodide and heating this with silver oxide:—



Ether is made on the large scale by heating sulphuric acid and alcohol in certain proportions, and then distilling the mixture with more alcohol as described below. Two distinct reactions are involved in this process. First, when alcohol and sulphuric acid are brought together, half the hydrogen of the acid is replaced by ethyl, thus:—



The product formed is called *ethylsulphuric acid* (*monoethyl sulphate*).

When ethylsulphuric acid is heated to about  $130^{\circ}$  with alcohol, ether is formed, and sulphuric acid is regenerated:—



The ether thus formed distils over; and, if alcohol is admitted to the mixture, ethylsulphuric acid will again be formed, and with excess of alcohol it will yield ether. The process is a continuous one, a small amount of sulphuric acid converting a large amount of alcohol into ether.

Ether is a colorless liquid of characteristic odor and taste. It boils at  $34.49^{\circ}$ . It melts at  $-117.6^{\circ}$ . Specific gravity, 0.71994 at  $15^{\circ}$ .

When its vapor is mixed with air, the mixture explodes violently when a flame is applied. Ether is somewhat soluble in water, and water is also somewhat, though less, soluble in ether; so that when the two are shaken together the volume of the ether becomes smaller, even though every precaution is taken to avoid evaporation. Ether mixes with alcohol in all proportions. It is a good solvent for resins, fats, alkaloids, and many other classes of carbon compounds.

It is frequently used to extract substances from aqueous solutions. It is used technically in the manufacture of collodion and in the purification of gun cotton.

It is an excellent anæsthetic, and is used extensively for this purpose. It was first used as an anæsthetic by Dr. Morton, a dentist of Boston, Mass., in 1846. When ether is brought upon the skin in the form of spray, the cold produced by the rapid evaporation is so great as to cause insensibility to pain.

*Manufacture of ether.* A mixture of 5 parts of alcohol (90 to 95 per cent) and 9 parts of concentrated sulphuric acid is heated in a still to  $127.5^{\circ}$ . Ether, water, and some alcohol distil over. Alcohol is run into the hot mixture in the still, so that the volume remains constant and the temperature is kept at  $127.5^{\circ}$ . Ether and water distil over. The crude ether contains some sulphur dioxide. It is washed with a solution of soda to remove this, and freed from alcohol and water by

distillation. This is the ether of commerce, used for most technical purposes. To remove all the water and alcohol the ether is distilled over sodium which combines with the water and the alcohol.

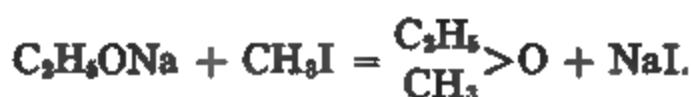
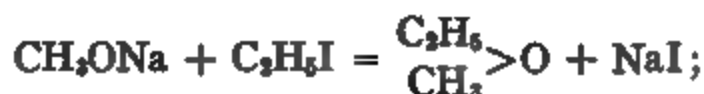
Chemical conduct of ether. Heated to  $150^{\circ}$  in a sealed tube with water containing a small amount of hydrochloric acid ether is converted into alcohol:—



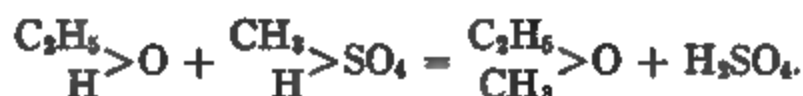
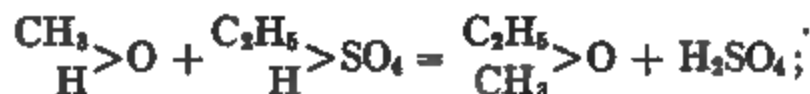
Treated with hydriodic acid, alcohol and iodoethane or iodoethane and water are formed:—



**Mixed ethers.**—Just as ethyl alcohol yields ethyl ether, and methyl alcohol yields methyl ether,  $(\text{CH}_3)_2\text{O}$ , by modifying the method, a *mixed ether*, *methyl ethyl ether*,  $\begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{smallmatrix} > \text{O}$ , can be obtained. This is formed by treating sodium methylate with iodoethane, or by treating sodium ethylate with iodomethane:—



It is formed also by distilling methyl alcohol with ethylsulphuric acid, or ethyl alcohol with methylsulphuric acid:—



Methyl ethyl ether is very similar to ordinary ether in its properties and reactions.

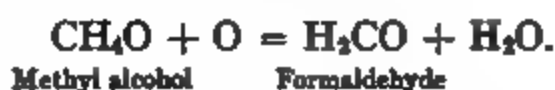
NOTE FOR STUDENT. Write out the reactions of methyl ethyl ether with water and with hydriodic acid. In the first reaction with hydriodic acid the methyl group combines with the iodine.

### 3. ALDEHYDES

It has been stated above that when methyl and ethyl alcohols are oxidized, they are converted into acids having the formulas  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_4\text{O}_2$ , respectively. By regulating the oxidation, products can be obtained intermediate between the alcohols and acids, and differing from the alcohols by two atoms of hydrogen. These products are called *aldehydes*, from *alcohol dehydrogenatum*, from the fact that they must be regarded as alcohols from which hydrogen has been abstracted. The relations in composition between the hydrocarbons, alcohols, aldehydes, and acids are shown by these formulas:—

Hydrocarbons	Alcohols	Aldehydes	Acids
$\text{CH}_4$	$\text{CH}_4\text{O}$	$\text{CH}_2\text{O}$	$\text{CH}_2\text{O}_2$
$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_6\text{O}$	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_2\text{H}_4\text{O}_2$

**Formic aldehyde, formaldehyde, methanal,  $\text{CH}_2\text{O}$ .**—This aldehyde is made by passing the vapor of methyl alcohol together with air over heated copper or silver wire gauze and collecting the gas in water:—



At ordinary temperatures it is a gas, which condenses when cooled to a liquid boiling at  $-21^\circ$ . It is manufactured on the large scale, and comes into the market in solution in water under the name of *formalin* and in the form of its solid polymer. Formalin contains from 35 to 40 per cent of formaldehyde.

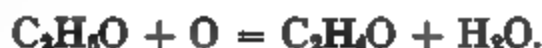
It is used in the manufacture of dyes (indigo, fuchsin, etc.), and pharmaceutical preparations (urotropine, formamint, etc.). On account of its germicidal powers it is very largely used as a disinfectant and as a preservative. It is also used in tanning, especially in the manufacture of sole leather, in waterproofing paper and textiles, and in the dyeing of fabrics; further, in photography for hardening the films, and recently in the manufacture of synthetic resins and plastics (*Bakelite* and *Condensite* from phenol and formaldehyde). These synthetic resins are used in the manufacture of phonograph records and

for many other purposes. Formaldehyde is also used in making mirrors.

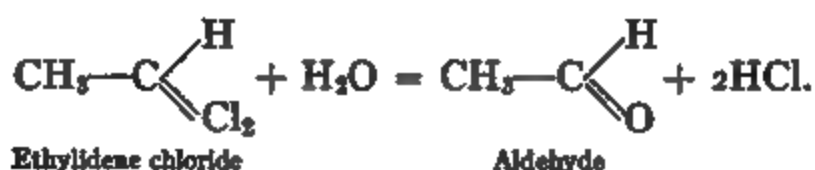
Although known since 1869, formaldehyde did not obtain technical importance until 1893 when it was first produced on the large scale. Since that time it has become one of the most important organic compounds, and new uses for it are constantly being found. When its solution in water is evaporated, a solid substance having the same composition as formic aldehyde is obtained. This is a polymeric variety, and is represented by the formula  $(\text{CH}_2\text{O})_x$ . It is called *paraformaldehyde*. When heated it gives formaldehyde.

In order to gain a clearer insight into the nature of the aldehydes, it will be best to study acetic aldehyde, the member of the group that has been longest known.

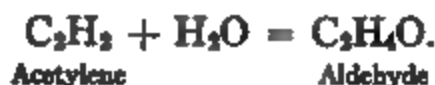
**Acetic aldehyde, ethanal,  $\text{C}_2\text{H}_4\text{O}$ .** — This aldehyde is formed whenever alcohol is brought in contact with an oxidizing mixture, as, for example, potassium bichromate and dilute sulphuric acid:—



Acetic aldehyde can be made by the action of water on ethylidene chloride:—



Aldehyde has been made commercially from acetylene:—



Large quantities of aldehyde are now obtained by fractional distillation of the first runnings from the rectification of crude wood alcohol. (See also 165.)

Aldehyde is a colorless liquid, boiling at  $20.8^\circ$ . It mixes with water and alcohol in all proportions. Its odor is marked and characteristic.

From the chemical point of view, the most characteristic property of aldehyde is its power to unite directly with other

substances. It unites with oxygen to form acetic acid; with hydrogen to form alcohol; with ammonia to form *aldehyde ammonia*,  $C_2H_4O.NH_3$ ; with hydrocyanic acid to form *aldehyde hydrocyanide*,  $C_2H_4O.HCN$ ; with the acid sulphites of the alkali metals, forming compounds represented by the formulas  $C_2H_4O.HKSO_3$  and  $C_2H_4O.HNaSO_3$ ; and with other substances. Indeed, if left to itself, it readily changes into polymeric modifications, uniting with itself to form more complex compounds, *paraldehyde* and *metaldehyde*.

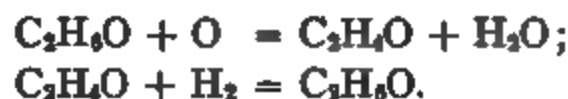
**Paraldehyde**,  $C_6H_{12}O_3$ . — This is formed by adding a drop of concentrated sulphuric acid to aldehyde, which causes the liquid to become hot. On cooling to  $0^\circ$ , paraldehyde solidifies in crystalline form. When pure it melts at  $12.59^\circ$ , dissolves in eight times its own volume of water, and boils at  $123-124^\circ$ . When distilled with sulphuric acid, hydrochloric acid, etc., it is converted into aldehyde. The weight of 22.4 liters of its vapor has been found to be 132.4, which means that its molecular weight is 132.4, and consequently its formula is  $(C_2H_4O)_3$ . It is a polymeric modification of aldehyde. It is used in medicine as an hypnotic and in the preparation of organic substances. Paraldehyde is the form in which aldehyde is bought and sold.

**Metaldehyde**. — Metaldehyde is formed together with paraldehyde, at a low temperature (below  $0^\circ$ ) by the action of hydrochloric acid gas. It crystallizes in needles, which are insoluble in water, and but slightly soluble in alcohol, chloroform, and ether in the cold, though more readily at a slightly elevated temperature. When heated to  $200^\circ$  in a sealed tube, it is completely converted into aldehyde. Determinations by the freezing point method show that the molecular weight of metaldehyde in phenol corresponds to the formula  $(C_2H_4O)_4$ . Distilled with dilute sulphuric acid, metaldehyde is converted into aldehyde.

Aldehyde is a strong reducing agent. When added to an ammoniacal solution of silver nitrate, metallic silver is deposited on the walls of the vessel in the form of a brilliant mirror. It is used commercially for making mirrors.

*Chemical transformations of aldehyde.* As aldehyde is pro-

duced from alcohol by oxidation, so alcohol can be formed from aldehyde by reduction:—



By oxidation aldehyde is converted into an acid of the formula  $\text{C}_2\text{H}_4\text{O}_2$ , which is acetic acid:—



Treated with phosphorus pentachloride, aldehyde yields *ethylidene chloride*,  $\text{C}_2\text{H}_4\text{Cl}_2$  (34). This reaction is of special interest and importance, as it helps us to understand the relation between aldehyde and alcohol. Alcohol, as has been shown, is ethyl hydroxide,  $\text{C}_2\text{H}_5\text{OH}$ . When oxidized it loses two atoms of hydrogen. Is the hydrogen of the hydroxyl one of the two which are given off? If so, what readjustment of the oxygen takes place? Such are the questions that suggest themselves.

To understand the action of phosphorus pentachloride on aldehyde, it will be necessary to examine briefly the action of this reagent upon compounds containing oxygen. When it is brought in contact with water, the change is represented by the equation:—



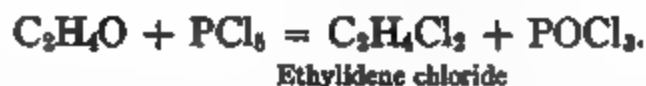
The phosphorus pentachloride gives up two atoms of chlorine and takes up oxygen in its place.

Now, when phosphorus pentachloride is brought together with an alcohol, a substituted water, a similar reaction takes place:—



Hydrochloric acid is given off, and ethyl chloride is formed, which is regarded as alcohol in which one chlorine atom takes the place of the hydroxyl. This is the kind of action that takes place whenever a chloride of phosphorus acts upon a compound containing hydroxyl; and hence the reaction is made use of for determining whether hydroxyl is present in a compound.

When aldehyde is treated with phosphorus pentachloride, the action is entirely different from that just described. Instead of one chlorine atom taking the place of a hydrogen and an oxygen atom, two chlorine atoms take the place of *the oxygen atom*: —



Ethylidene chloride

If the explanation above offered of the action of phosphorus pentachloride on water and on alcohol is correct, it follows that aldehyde is not a hydroxyl compound. We can readily understand why two chlorine atoms should take the place of the oxygen atom, if the latter is in combination only with carbon as in the group  $>\text{CO}$ . There is an essential difference between this kind of combination and that which we have in hydroxyl as  $\equiv\text{C}-\text{O}-\text{H}$ . In the latter condition the oxygen serves to connect carbon with hydrogen; in the former it is in combination only with the carbon, and, presumably, the energy which holds it can also hold two atoms of chlorine or of any other univalent element with which it can unite. So that, if oxygen is present in a compound combined only with carbon, we should expect two chlorine atoms to take its place when the compound is treated with phosphorus pentachloride. Let  $\text{R}_2\text{CO}$  represent any such compound; then we should have: —



while, when oxygen is present in the hydroxyl condition, we should have: —

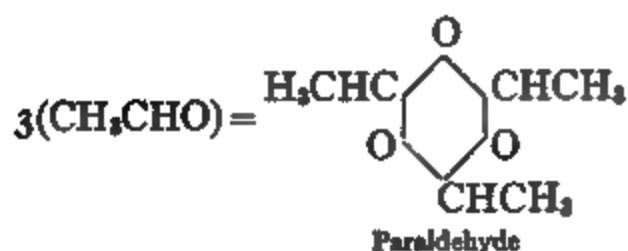
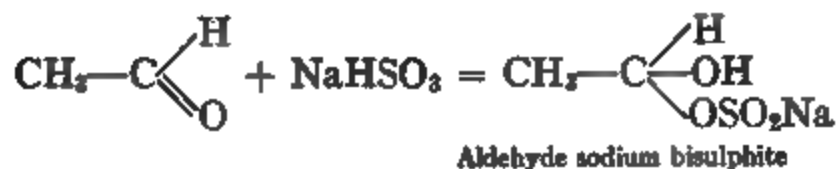
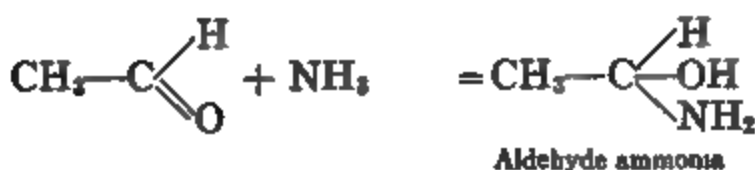
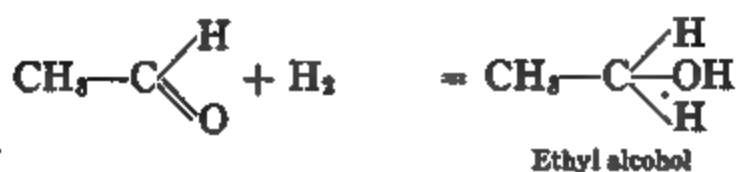


Just as the latter reaction is used to detect the presence of hydroxyl oxygen, so the former is used to detect oxygen in the other condition, which is commonly known as the *carbonyl* condition.

In terms of the valence hypothesis, it is said that in the hydroxyl compounds oxygen is in combination with carbon with one of its affinities, and with hydrogen with the other, while in the carbonyl compounds it is in combination with carbon with both its affinities as represented thus,  $>\text{C}=\text{O}$ .



According to the above reasoning aldehyde is a carbonyl compound, or it contains the bivalent group  $>\text{C}=\text{O}$ . The simplest aldehyde must therefore be represented by the formula  $\text{H}_2\text{C}=\text{O}$ . Its homologue, acetic aldehyde, is  $\text{CH}_3\text{HC}=\text{O}$ . The characteristic properties of aldehyde are due to the presence of this group,  $-\text{HC}=\text{O}$ , which is called the aldehyde group. That aldehyde does not contain a hydroxyl group is also shown by the fact that it does not form esters with acids as alcohol does. That the formula  $\text{CH}_3\text{C}\begin{smallmatrix} \text{H} \\ \diagup \\ \text{O} \end{smallmatrix}$  is in accord with the chemical conduct of aldehyde is shown by the reactions represented below:—



**Chloral, trichloraldehyde,  $\text{CCl}_3\text{CHO}$ .** — When chlorine acts upon aldehyde, in the presence of water and calcium carbonate, substitution takes place, and *trichloraldehyde* is formed. When alcohol is treated with chlorine, a double action takes place. The alcohol is first changed to aldehyde thus: —



Then the chlorine acts upon the aldehyde, and is substituted for the three hydrogens of the methyl, forming trichloraldehyde: —



In reality the aldehyde first formed combines with the alcohol, forming an intermediate product which is acted upon by the chlorine; and the chlorine product thus formed is decomposed with concentrated sulphuric acid, forming chloral. The essential features of the reaction, however, are stated in the above equations. Trichloraldehyde is the substance commonly known as chloral. It has all the general properties of aldehyde, and the conclusion is therefore justified that it contains the

aldehyde group  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—CH} \end{array}$ .

Chloral is a colorless liquid, which boils at  $98^\circ$ , and has the specific gravity 1.54 at  $0^\circ$ .

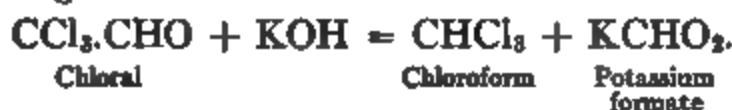
**NOTE FOR STUDENT.** — Give the formulas of compounds formed when chloral is brought together with ammonia, hydrocyanic acid, and the acid sulphites of the alkali metals. What is the formula of the acid formed by its oxidation? The answer is given in the statement that the general chemical conduct of chloral is the same as that of aldehyde.

When chloral and water are brought together, they unite with evolution of heat to form a crystalline compound, *chloral hydrate*,  $\text{CCl}_3\text{CHO} + \text{H}_2\text{O}$ , which is easily soluble in water, and crystallizes from the solution in beautiful, colorless, monoclinic prisms. It melts at  $47.4^\circ$  and boils at  $97.5^\circ$ , dissociating into chloral and water. Taken internally in doses of from 0.6 to 2<sup>g</sup>, it causes sleep. In larger doses it acts as an anæsthetic. It is a habit-forming drug.

Chloral hydrate is an example of a compound in which one

carbon holds two hydroxyls in combination,  $\text{HC} \begin{array}{l} \text{CCl}_3 \\ | \\ \text{OH} \\ | \\ \text{OH} \end{array}$ .

When heated with an alkali, chloral and chloral hydrate break down, yielding chloroform and a formate: —



NOTE FOR STUDENT. — How is chloroform made from alcohol? How is the method explained? Answer the same questions for iodoform. The bleaching powder used in preparing chloroform furnishes chlorine. Is a base present?

#### 4. ACIDS

When methyl and ethyl alcohols are oxidized, they are converted first into aldehydes, and then the aldehydes take up oxygen and are converted into acids. The relations in composition between the hydrocarbons, alcohols, aldehydes, and acids are shown in the subjoined table: —

Hydrocarbons	Alcohols	Aldehydes	Acids
$\text{CH}_4$	$\text{CH}_3\text{O}$	$\text{CH}_2\text{O}$	$\text{CH}_2\text{O}_2$
$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{O}$	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_2\text{H}_4\text{O}_2$

The two acids whose formulas are here given are the well-known substances, *formic* and *acetic acids*.

**Formic acid, methane acid,  $\text{CH}_2\text{O}_2$ .** — This acid occurs free in nature in red ants (*formica rufa*), in stinging nettles, in fir cones, in some fruits, in honey, and in perspiration, urine, and extract of meat. It is said that the pain and swelling caused by the stinging of bees, hornets, and wasps is due to the injection of a small amount of formic acid.

It can be obtained by distilling red ants. It is best prepared in the laboratory by heating oxalic acid with glycerol. Oxalic acid has the composition represented by the formula  $\text{C}_2\text{H}_2\text{O}_4$ . When heated in glycerol to  $100^\circ - 110^\circ$  it breaks down into carbon dioxide and formic acid (159): —



The formic acid distils over at this temperature into the receiver.

The formation of formic acid by oxidation of methyl alcohol, and by treatment of chloral with an alkali, has already been mentioned. The following methods are of special interest:—

(1) By the action of carbon monoxide on sodium hydroxide:—



This method is used for the preparation of sodium formate on the large scale. When producer gas (containing about 30 per cent carbon monoxide) is heated to  $120^\circ$ – $130^\circ$  under a pressure of 6 to 8 atmospheres with solid sodium hydroxide, sodium formate is formed.

(2) By the action of metallic potassium upon moist carbon dioxide:—



(3) By treatment of a concentrated solution of ammonium carbonate with sodium amalgam:—



According to these two methods formic acid appears as a reduction product of carbonic acid formed by the abstraction of one atom of oxygen:—



It will be shown that all organic acids may be regarded as derivatives of either formic acid or carbonic acid.

(4) When hydrocyanic acid is heated with a dilute mineral acid or with a solution of an alkali, it gives ammonia and formic acid:—



Of course, if a mineral acid is present, the ammonium salt of this acid is formed; and, if an alkali is present, the formate of the alkali metal results. *A reaction similar to this is used very extensively in the preparation of the organic acids, as will be shown.*

Anhydrous formic acid can be made by dehydrating either the copper or lead salt, and passing dry hydrogen sulphide

over the salt heated to  $130^{\circ}$ , or by heating a mixture of dry sodium formate and sodium acid sulphate:—



It is a colorless liquid boiling at  $100.8^{\circ}$  at  $760^{\text{mm}}$ . It has an irritating, acrid odor. Dropped on the skin, it causes extreme pain and produces blisters. Its specific gravity at  $0^{\circ}$  is 1.24. When cooled down it solidifies to a mass of crystals which melt at  $8.3^{\circ}$ . It is a much stronger acid than acetic acid. It is a powerful antiseptic, and is hence used to preserve fruit juices. As it is now made very cheaply, it is displacing acetic acid and other acids in the manufacture of leather, in dyeing textiles, and for other purposes.

Concentrated sulphuric acid decomposes it into carbon monoxide and water:—



It is easily oxidized to carbonic acid. Hence it acts as a reducing agent. Heated with the oxides of mercury or silver, they are reduced to the metallic condition:—



Like other acids, formic acid yields a large number of salts with bases, and ethereal salts or esters with the alcohols. The salts are all soluble in water, and some of them, as the lead, copper, and barium salts, crystallize very well. Some of the esters will be mentioned when these substances are taken up as a class.

**Acetic acid, ethane acid,  $\text{C}_2\text{H}_4\text{O}_2$ .**—Acetic acid in the form of wine vinegar was known to the ancients. It is found in the free condition and in the form of salts in plant juices and in the perspiration, milk, muscles, and excrement of animals. Esters of acetic acid also occur in nature as, for example, triacetin in croton oil.

Acetic acid is made

- (1) By the oxidation of alcohol; and
- (2) By the distillation of wood.

When pure alcohol is exposed to the air it undergoes no change. If, however, some platinum black is placed in it, oxidation takes place and acetic acid is formed. So also if fermented liquors that contain nitrogenous substances are exposed to the air, oxidation takes place, and the liquor becomes sour in consequence of the formation of acetic acid. A great deal of acetic acid is made by exposing cider or wine to the action of the air. The product is known as *cider* or *wine vinegar*. The formation of vinegar has been shown to be due to the action of a microscopic organism (*Bacterium aceti*) present in "mother-of-vinegar." This serves in some way to convey the oxygen from the air to the alcohol. The "quick-vinegar process," much used in the manufacture of vinegar, consists in allowing weak alcohol to pass slowly through vats filled with wood shavings which have become covered with *Bacterium aceti*. The presence of the organism is secured by first pouring strong vinegar into the vats, and allowing it to stand for one or two days in contact with the shavings. Air is admitted near the bottom of the vats.

When wood is distilled, the aqueous distillate contains wood alcohol, acetone, and acetic acid. By keeping the temperature down comparatively low, the amount of acetic acid obtained is increased. The distillate is neutralized with lime, the wood alcohol and acetone distilled off, and the solution of crude calcium acetate thus obtained evaporated to dryness. It is then treated with concentrated sulphuric acid, and the acetic acid distilled off under diminished pressure.

The crude acid containing 80 per cent acetic acid is fractionated in column stills and an acid containing 98.99 per cent acetic acid obtained. The chemically pure acetic acid is made from this by adding potassium permanganate, to oxidize impurities, and distilling.

Acetic acid was also manufactured on the large scale during the World War by the oxidation of acetic aldehyde made from acetylene, and also by the oxidation of ethyl alcohol.

It is used in medicine in the form of its salts, in the manufacture of synthetic remedies, such as antipyrine, aspirin, anti-

febrin, phenacetin, tannigen, acetic ether, etc.; in the preparation of artificial perfumes and extracts, such as ionone, coumarin, vanillin, etc.; in the preparation of synthetic dyes, as indigo, and of intermediates, as paranitroaniline; of solvents, as acetin; and in the preparation of mordants used in dyeing; in the form of its calcium salt in the manufacture of acetone; and for a great variety of other purposes. Vinegar, according to the pure food law, must contain 4 grams acetic acid in 100<sup>cc</sup>. Acetic acid is a preservative and in the form of vinegar it is largely used for this purpose in making pickles, chow chow, tomato catsup, etc.

There are three other methods which may be used for making acetic acid. They are:—

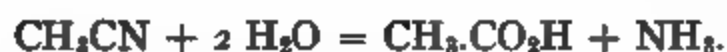
(1) By heating sodium methylate with carbon monoxide:—



(2) By heating carbon dioxide with *sodium methyl*:—



(3) By heating methyl cyanide,  $\text{CH}_3\text{CN}$ , with a dilute mineral acid or a solution of an alkali:—



This reaction is analogous to that involved in the formation of formic acid from hydrocyanic acid. These reactions show the presence of a methyl group in acetic acid.

Pure acetic acid is a colorless liquid that boils at 118.7°. It has a very penetrating, pleasant, acid odor, and a sharp acid taste. *The pure substance acts upon the skin like formic acid, causing pain and raising blisters.* It solidifies when cooled down, and the crystals melt at 16.54°. The pure acid, which is solid at temperatures below 16°, is known as *glacial acetic acid*. Its specific gravity is 1.08 at 0°. It mixes with water in all proportions. Glacial acetic acid is an excellent solvent for many organic substances, and is therefore frequently used in scientific research.

*Derivatives of acetic acid.* Acetic acid yields a large number of derivatives. They may be presented briefly under two

heads: (1) Those which are formed in consequence of the acid properties and which necessitate a loss of the acid properties, as the salts, ethereal salts, chloride, and anhydride; and (2) those in which the acid properties remain unchanged, as the chloroacetic acids.

*Salts of acetic acid.* The acetates of the alkalies were the first compounds of carbon ever prepared. The *potassium* and *sodium* salts are used in medicine and in the chemical laboratory. Both crystallize, the sodium salt particularly well.

*Calcium acetate*,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2 \text{H}_2\text{O}$ . This salt, in the impure form, known as "gray acetate of lime," is the product obtained when the aqueous distillate from wood is treated with lime and the solution (after distilling off the wood alcohol and acetone) is evaporated to dryness. It is the material from which acetic acid and acetone are made on the large scale. Thousands of tons of it are made annually, mostly in the United States.

*Lead acetate*,  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Pb} + 3 \text{H}_2\text{O}$ . This salt, which is commonly known as *sugar of lead*, is made on the large scale by dissolving lead oxide in acetic acid. It crystallizes well, and is soluble in 1.5 parts of water at ordinary temperatures. Commercial sugar of lead frequently contains an excess of lead oxide in the form of basic salts. A solution of such a mixture becomes turbid when allowed to stand in the air, or gives a precipitate when dissolved in ordinary spring water, in consequence of the formation of lead carbonate.

Lead acetate is used as a reagent in the laboratory, as it is one of the few soluble salts of lead. Like all soluble salts of lead it is poisonous. Technically it is used in the manufacture of chrome yellow, white lead, and other lead compounds.

*Cupric acetate*,  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu} + \text{H}_2\text{O}$ . This salt is made by dissolving basic copper carbonate in acetic acid. It crystallizes in blue-green, transparent prisms. A *basic acetate*, formed by the action of acetic acid and air on copper, is known as *verdigris*.

*Cupric acetoarsenite*,  $3 \text{Cu}(\text{AsO}_2)_2 + (\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}$ . This double salt is made on the large scale by precipitating a hot solution of sodium arsenite with a solution of copper sulphate and then adding dilute acetic acid. It has a fine bright green color,

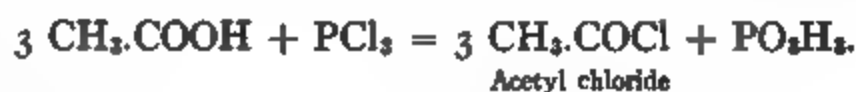


and is used as a pigment and as an insecticide. It is the chief constituent of Emerald green, Paris green, or Schweinfurt green.

Iron forms two distinct salts with acetic acid, the *ferrous* salt,  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Fe} + 4 \text{H}_2\text{O}$ , and the *ferric* salt,  $(\text{C}_2\text{H}_3\text{O}_2)_3\text{Fe} + 2\text{H}_2\text{O}$ . The latter is formed when sodium acetate is added to a neutral solution of a ferric salt. At first the solution becomes deep-red in color, owing to the formation of ferric acetate; but, on boiling, all the iron is precipitated as ferric hydroxide and acetic acid is set free. Hence this salt is used for the purpose of separating iron from manganese, zinc, cobalt, and nickel in analytical operations. Aluminium and chromium acetates are decomposed in the same way as ferric acetate.

The ethereal salts will be mentioned briefly when this class of compounds is taken up. The principal one is *ethyl acetate* or *acetic ether*, which is formed from acetic acid and ordinary alcohol. When a mixture of these two substances is heated with a small quantity of sulphuric acid, the ester is formed and can be recognized by its pleasant odor. This reaction is used for the detection of acetic acid.

**Acetyl chloride,  $\text{CH}_3\text{COCl}$ .**—Just as alcohol, when treated with phosphorus trichloride, yields ethyl chloride, so acetic acid, when treated with the same reagent, yields acetyl chloride. The two reactions are perfectly analogous. They consist in the substitution of chlorine for hydroxyl:—



Instead of phosphorus trichloride it is better to use thionyl chloride:—



On the large scale sulphuryl chloride is used:—

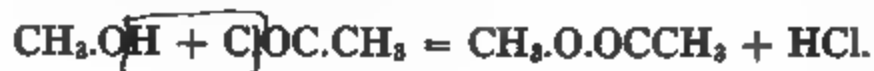


Acetyl chloride is a colorless liquid which boils at  $51^\circ$ . Water acts upon it very readily, acetic and hydrochloric acids being formed:—



In this case the chlorine is replaced by hydroxyl. As the substance is volatile, it fumes in contact with the moisture of the air in consequence of the formation of hydrochloric acid. It must hence be kept in tightly stoppered bottles. In handling it, care must be taken not to bring it near the nose, as the vapor is suffocating, and it attacks the mucous membrane of the eyes and nose, producing coughing and other bad results.

Acetyl chloride is a valuable reagent much used in the investigation of compounds of carbon. Its value depends upon its action towards alcohols. When it is brought together with an alcohol, as, for example, methyl alcohol, hydrochloric acid is evolved, and the acetyl group takes the place of the hydrogen of the alcoholic hydroxyl:—



The product is an ethereal salt, methyl acetate. This kind of action takes place whenever an alcohol is treated with acetyl chloride. Hence, if on treating a substance with acetyl chloride, an acetate is formed, showing that hydrogen is replaced by acetyl, the conclusion is justified that the substance contains alcoholic hydroxyl.

Acetyl chloride is also used in making acetophenone and acetyl derivatives.

**Acetic anhydride, acetyl oxide,  $\text{C}_4\text{H}_6\text{O}_3$ .**—This is made by abstracting water from the acid. Like most other organic acids, acetic acid contains hydroxyl, as has been shown above. It may hence be represented thus:  $\text{CH}_3\text{COOH}$ . The group  $\text{CH}_3\text{CO}$  is known as acetyl. Now when water is abstracted from the acid, the change represented in this equation takes place:—



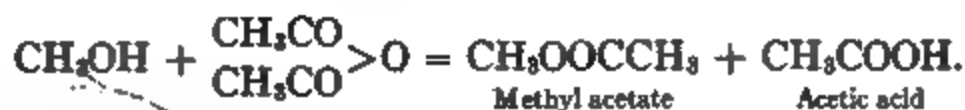
Hence, according to this, acetic anhydride appears as the oxide of acetyl, while the acid itself is the hydroxide. Acetic anhydride is made in this way on the large scale, sulphur chloride being used as the dehydrating agent.

It is prepared in the laboratory by heating sodium acetate with acetyl chloride:—



Acetic anhydride is a colorless liquid which boils at  $136.4^\circ$ . Boiled with water it gives acetic acid.

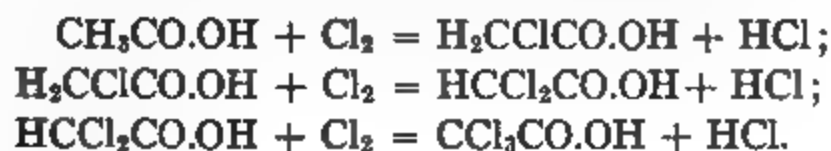
Acetic anhydride is also used as a reagent for detecting alcoholic hydroxyl. With methyl alcohol, for example, it acts as shown in the following equation:—



With all substances that contain alcoholic hydroxyl the same kind of action takes place.

Acetic anhydride is used principally in the manufacture of acetyl cellulose. It is also used in making synthetic remedies, perfumes, dyes, etc.

*Halogen substitution products of acetic acid.* These bear the same relation to acetic acid that the substitution products of marsh gas bear to marsh gas. They are formed by the simple substitution of a halogen for hydrogen. Only three of the four hydrogen atoms of acetic acid are capable of direct replacement by halogen—the three in the methyl group. The fourth is the one to which the acid properties are due. Hence the substitution products are acids. The best-known of these are the chloroacetic acids, which are made by treating the acid with chlorine in the presence of a chlorine carrier, as sulphur. They are *monochloroacetic*, *dichloroacetic*, and *trichloroacetic acids*. Their formation is represented by the following equations:—



Monochloroacetic acid is also made from acetylene on the large scale (299).

When treated with nascent hydrogen they are converted into acetic acid. They yield salts, ethereal salts, anhydrides, etc., just the same as acetic acid itself.

*Monochloroacetic acid* is a crystalline solid melting at  $63^{\circ}$  and boiling at  $186^{\circ}$ . It is used in the manufacture of synthetic indigo.

*Dichloroacetic acid* is also made by boiling chloral hydrate with a solution of potassium cyanide:—

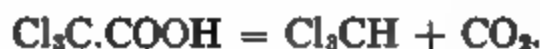


It is a liquid boiling at  $191^{\circ}$ .

*Trichloroacetic acid* is a solid melting at  $57^{\circ}$  and boiling at  $195^{\circ}$ . It is formed very readily by oxidizing chloral with nitric acid:—



When boiled with water it gives carbon dioxide and chloroform:—



NOTE FOR STUDENT. Compare this reaction with the one used to prepare marsh gas from sodium acetate (22).

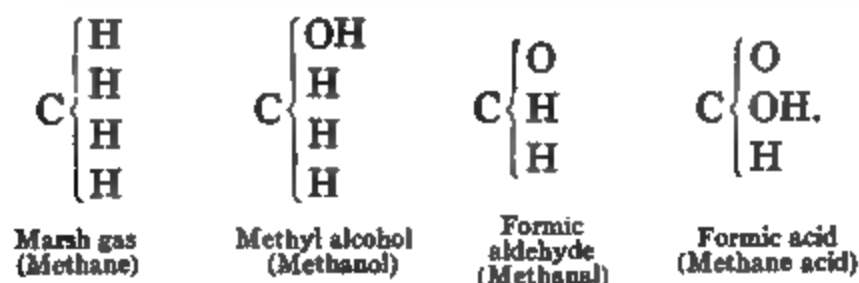
The chloroacetic acids are *very much stronger* acids than acetic acid. This is due to the introduction of the negative chlorine atoms. Trichloroacetic acid is comparable in strength with the mineral acids.

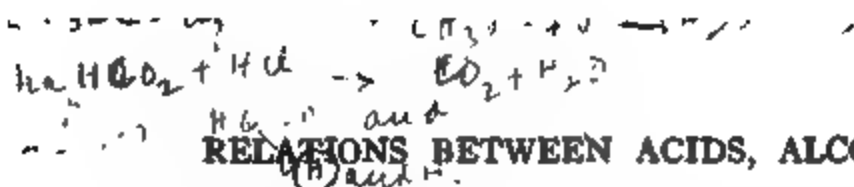
*Theory in regard to the relations between the acids, alcohols, aldehydes, and hydrocarbons.* The reactions and methods of formation of acetic acid enable us to form a clear conception of the relation of its constituents. In the first place the presence of hydroxyl is shown by the reaction with phosphorus trichloride. We hence have  $\text{C}_2\text{H}_3\text{O}.\underline{\text{OH}}$  as the formula representing this fact. But several questions still remain to be answered. There is another oxygen atom to be accounted for; and the relations between the hydroxyl and this oxygen must be determined if possible. The fact that this second oxygen is not replaced by chlorine when acetyl chloride is treated with phosphorus trichloride indicates that it is not present as hydroxyl, and all methods of testing for hydroxyl fail to show its presence in acetyl chloride. Hence we may conclude that the second oxygen atom is present as carbonyl, CO. This leads

us to the formula  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$  for the simplest acid, or formic acid. Accordingly, formic acid appears as carbonic acid,  $\text{O}=\text{C}<\overset{\text{OH}}{\text{OH}}$ , in which one hydroxyl has been replaced by hydrogen. It has already been shown that this reduction can be accomplished without difficulty and that carbonic acid is the oxidation product of formic acid. Now, as acetic acid is the homologue of formic acid, there is good reason to believe that it differs from the latter in that it contains methyl in place of the hydrogen, which is in direct combination with carbon, and this view is confirmed by the fact that acetic acid can be made from sodium methyl,  $\text{CH}_3\text{Na}$ , from sodium methylate,  $\text{NaOCH}_3$ , and from methyl cyanide,  $\text{CH}_3\text{CN}$ . The acid

must hence be represented by the formula  $\text{CH}_3\cdot\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  or  $\text{OC}<\overset{\text{CH}_3}{\text{OH}}$ . The common constituent of the two acids is the

group  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$  or  $-\text{CO.OH}$ , which is known as *carboxyl*. Acetic acid is closely related not only to formic but to carbonic acid. It may be regarded as carbonic acid,  $\text{OC}<\overset{\text{OH}}{\text{OH}}$ , in which one hydroxyl is replaced by the radical methyl. In a similar way we shall see that all organic acids are to be regarded as derived either from formic acid or from carbonic acid. Representing now the simplest hydrocarbon, alcohol, aldehyde, and acid, by the structural formulas deduced from the facts, we have:



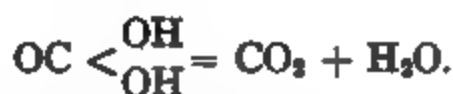


Methyl alcohol cannot be made from marsh gas by oxidation, but by making chloromethane,  $\text{CH}_3\text{Cl}$ , then substituting hydroxyl,  $\text{OH}$ , for chlorine we get methyl alcohol. Here we have replaced one hydrogen of marsh gas by hydroxyl,  $\text{OH}$ . Starting with methyl alcohol, we might expect the next change caused by oxidation to consist in the introduction of another

oxygen atom, giving a compound  $\text{C} \begin{Bmatrix} \text{OH} \\ \text{OH} \\ \text{H} \\ \text{H} \end{Bmatrix}$ . But it has been found that, except under certain conditions (54), one carbon atom cannot hold two hydroxyls in combination, and that, if such a compound is formed, it loses the elements of water, thus,



This kind of change is illustrated in the formation of carbon dioxide from the salts of carbonic acid when they are treated with acids. Instead of getting the acid  $\text{OC} < \begin{Bmatrix} \text{OH} \\ \text{OH} \end{Bmatrix}$ , which we should naturally expect, we get this minus water:—



Now, when the aldehyde is oxidized, another oxygen atom is introduced, and the substance thus produced is formic acid, for the hydroxyl hydrogen can be replaced by metals, and has in general the characteristics of acid hydrogen. Carbon in combination with oxygen as carbonyl, and at the same time with hydroxyl, gives the compound containing it acid properties.

If, finally, formic acid  $\text{C} \begin{Bmatrix} \text{O} \\ \text{OH} \\ \text{H} \end{Bmatrix}$  is oxidized, it is probable that

the same change takes place as when the alcohol is oxidized.



## 66 DERIVATIVES OF METHANE AND ETHANE

That is to say, the hydrogen is oxidized to hydroxyl, when a compound containing two hydroxyls in combination with one carbon atom would be the result. This is carbonic acid. But this breaks down into water and carbon dioxide, which are the products of oxidation of formic acid.

All the many representatives of the great classes of carbon compounds known as the hydrocarbons, alcohols, aldehydes, and acids are derived from the four fundamental substances, methane, methyl alcohol, formic aldehyde, and formic acid. Replace one of the hydrogen atoms of methane by a radical, like methyl,  $\text{CH}_3$ , and we get a new hydrocarbon, which may be

represented by the formula  $\text{C} \begin{Bmatrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{R} \end{Bmatrix}$ . If a radical is substituted

for one of the hydrogen atoms of the methyl group of methyl

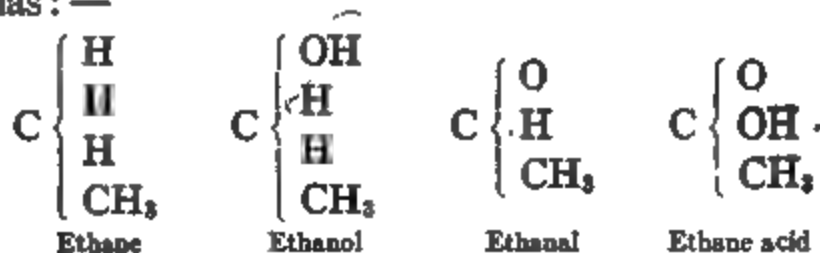
alcohol, a new alcohol is formed,  $\text{C} \begin{Bmatrix} \text{OH} \\ \text{H} \\ \text{H} \\ \text{R} \end{Bmatrix}$ . So also a similar re-

placement of a hydrogen atom in formic aldehyde by a radical

gives a new aldehyde,  $\text{C} \begin{Bmatrix} \text{O} \\ \text{H} \\ \text{R} \end{Bmatrix}$ ; and, finally, the organic acids

may be represented by the formulas  $\text{C} \begin{Bmatrix} \text{O} \\ \text{OH} \\ \text{R} \end{Bmatrix}$ , or  $\text{OC} < \begin{Bmatrix} \text{R} \\ \text{OH} \end{Bmatrix}$ ,

which show their relations to formic and carbonic acids. Thus ethane, ethyl alcohol, acetic aldehyde, and acetic acid, in which the radical is methyl,  $\text{CH}_3$ , are represented by these formulas:—

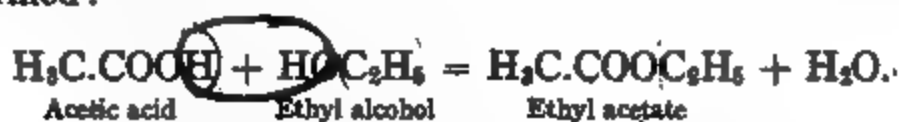


Hereafter the structural formulas of the alcohols, aldehydes,

and acids will be represented by writing the hydroxyl group OH, the aldehyde group CHO, and the carboxyl group CO.OH or CO<sub>2</sub>H, separately from the rest of the formula.

### 5. ETHEREAL SALTS OR ESTERS—ESTERIFICATION

It has already been shown that alcohols react with mineral acids to give esters, analogous to the salts of the univalent metals, in which the acid hydrogen is replaced by the radical methyl or ethyl. In the same way esters of the organic acids are formed:—



Owing to the fact that the alcohols are weak bases and that the organic acids are weak acids and that neither are ionized to any extent, this reaction proceeds slowly, requiring several hours to reach equilibrium at the boiling point, whereas the neutralization of acetic acid by sodium hydroxide solution is instantaneous:—



The reaction between *any* acid and an alcohol is also a *reversible* one, as the water formed hydrolyzes the ester to acid and alcohol:—



consequently a state of equilibrium is reached after a time and the reaction never proceeds to completion, as in the case of the neutralization of an acid by an alkali. For example, if equivalent quantities of acetic acid and ethyl alcohol are used, only about 66 per cent of the acid can be converted into the ester. In order to increase the velocity of the reaction and to obtain a larger yield of the ester, a catalytic agent is used, either a small amount of dry hydrochloric acid or concentrated sulphuric acid. It is customary to heat the organic acid with methyl or ethyl alcohol, containing about 3 per cent of dry



hydrochloric acid gas, to the boiling point for about three hours.

The sulphuric acid, when used as a catalyst, unites with the alcohol:—



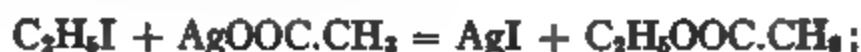
to form ethylsulphuric acid, which then reacts with the organic acid to give the ester, regenerating the sulphuric acid, which again reacts with more alcohol:—



This process with sulphuric acid is analogous to the formation of ether and hence the esters are frequently called ethereal salts or compound ethers. A 90 to 95 per cent yield of the ester can generally be obtained by the catalytic method of esterification. The esters are separated from the excess of alcohol and acids by pouring the mixture into water in which the esters are generally insoluble.

Two other methods of preparing the esters have already been given. These involve the action of the chloride of the acid or of the acid anhydride on the alcohols (61, 62).

Another method is to heat a salt of the acid (usually the silver salt) with methyl or ethyl iodide:—



or the sodium salt is treated with dimethyl or diethyl sulphate:—

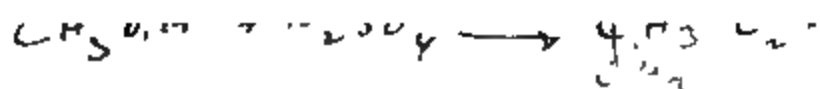


In these reactions the metal is directly replaced by the radical and thus the relation between the metallic salts and the ethereal salts is clearly established.

These methods of preparing ethereal salts are of general application and are used when an ester cannot readily be obtained by the catalytic method.

Among the more important methyl and ethyl esters, the following may be mentioned:—

**Methylsulphuric acid,**  $\begin{matrix} \text{CH}_3\text{O} \\ \text{HO} \end{matrix} > \text{SO}_3$ , formed by heating methyl



## ETHYLSULPHURIC ACID

69

alcohol and sulphuric acid on the water bath. The acid itself, as well as its salts, is very easily soluble in water. Anhydrous methylsulphuric acid is made by the action of sulphur trioxide on anhydrous methyl alcohol:—



**Dimethyl sulphate,  $(CH_3O)_2SO_2$ .**—When anhydrous methylsulphuric acid is distilled in a vacuum, dimethyl sulphate passes over and sulphuric acid is left behind:—

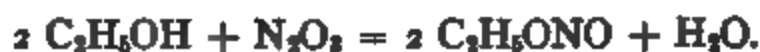


It is an oily liquid, boiling at  $188.3^\circ$ – $188.6^\circ$ , insoluble in water, and is *very poisonous*. It is largely used instead of the more expensive methyl iodide for the purpose of introducing methyl groups into organic compounds (68). Dimethyl sulphate is also made by absorbing dimethyl ether (a by-product of the manufacture of dimethylaniline) in fuming sulphuric acid:—



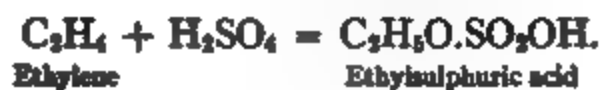
**Ethyl nitrate,  $C_2H_5ONO_2$ ,** is made by treating alcohol with nitric acid, adding urea to decompose any nitrous acid formed. Unless precautions are taken in mixing these reagents, oxidation of the alcohol will take place, and a violent explosion may result.

**Ethyl nitrite,  $C_2H_5O.NO$ ,** boiling at  $17^\circ$ , results from the action of the anhydride of nitrous acid on alcohol:—



An alcoholic solution of ethyl nitrite is known as “sweet spirit of nitre.”

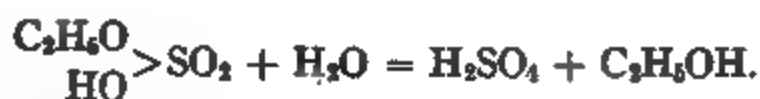
**Ethylsulphuric acid,  $C_2H_5O.SO_3OH$ ,** is made in the same way as the methyl compound. Ethylsulphuric acid is formed when ethylene is absorbed in concentrated sulphuric acid:—



The potassium salt is used in preparing ethyl compounds. Thus, ethyl bromide results from the distillation of potassium bromide and potassium ethylsulphate:—



The acid and its salts are easily soluble in water. When boiled with water, it is hydrolyzed, yielding alcohol and sulphuric acid:—



Diethyl sulphate,  $(\text{C}_2\text{H}_5\text{O})_2\text{SO}_2$ , is made by distilling anhydrous ethylsulphuric acid or, better, its dry sodium salt in a vacuum:—



It is a colorless liquid, insoluble in water, which solidifies at  $-24.5^\circ$ , and is poisonous. It is used for the purpose of introducing ethyl groups into organic compounds.

Phosphoric acid yields *triethyl phosphate*,  $(\text{C}_2\text{H}_5)_3\text{PO}_4$ , *diethylphosphoric acid*,  $(\text{C}_2\text{H}_5)_2\text{HPO}_4$ , and *ethylphosphoric acid*,  $\text{C}_2\text{H}_5\text{H}_2\text{PO}_4$ .

There are also similar derivatives of arsenic, boric, silicic, and other mineral acids.

Of the ethereal salts which the two alcohols form with formic and acetic acids, *ethyl formate* and *ethyl acetate* are the best-known. The methods of preparing them have already been given. They are both liquids having pleasant odors. This is indeed a characteristic of many of the volatile ethereal salts of the organic acids, and many of the odors of fruits and flowers are due to the presence of one or another of these compounds. Many of them are used in perfumery and for flavoring purposes instead of the natural substances.

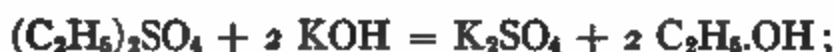
Ethyl formate,  $\text{H} \cdot \text{COOC}_2\text{H}_5$ , boiling point  $55^\circ$ , is used in making artificial rum or arrack and in the synthesis of organic compounds.

**Ethyl acetate, acetic ether,  $\text{CH}_3\text{COOC}_2\text{H}_5$** , boiling at  $75^\circ$ , is made on the large scale and extensively used as a solvent for nitrocellulose and cellulose acetate in the manufacture of photographic films, leather substitutes, and a number of other products.

*Saponification of ethereal salts.* Salts of most metals are instantaneously decomposed when treated with a solution of an alkaline hydroxide, as caustic soda or caustic potash, the result being a salt of the alkali metal and the hydroxide of the replaced metal, as seen in the case of copper sulphate and sodium hydroxide : —



So also the ethereal salts are similarly decomposed when treated with solutions of the alkalies, though not as readily as salts. It is usually necessary to boil the ethereal salt with a solution of the alkali when decomposition takes place, the radical, like the metal, appearing in the form of the hydroxide or alcohol, and the alkali metal taking its place. Thus, when ethyl sulphate is heated with a solution of caustic potash, this reaction takes place : —



and when ethyl acetate is heated with caustic soda, we have this reaction : —



All ethereal salts are decomposed by boiling with the caustic alkalies. As this decomposition is best known on the large scale in the preparation of soaps, it is commonly called *saponification*. As will be shown, the fats are ethereal salts, and soap-making consists in hydrolyzing fats by means of the caustic alkalies. Hence, generally, to *saponify* an ethereal salt means to hydrolyze it by means of an alkali into the corresponding alcohol and the alkali salt of the acid contained in it.

The ethereal salts are also hydrolyzed by heating them with dilute mineral acids : —



Secondary alcohol  $\rightarrow$  0 ketone  $\xrightarrow{C_{17}}$

## 6. KETONES OR ACETONES

When calcium or barium acetate is distilled, a liquid passes over which has the composition  $C_3H_6O$ , and a carbonate remains behind. The reaction has been carefully studied, and has been shown to take place in accordance with the following equation:—



The formula  $H_3CCOCH_3$  represents the compound *acetone*. It is the best-known representative of a class of compounds called *ketones*.

**Acetone, dimethylketone, propanone,  $H_3CCOCH_3$ .**— This substance has long been known as a product of the distillation of acetates. It is present in considerable quantities in the products of the distillation of wood, and is separated from the mixture after the removal of the acetic acid. It also occurs in the blood and in urine in small quantity. In certain pathological conditions it occurs in relatively large quantities in the urine, as in *acetonuria* and in *diabetes mellitus*.

It can be purified by shaking a mixture containing it with a concentrated solution of monosodium sulphite. It unites with the salt, forming a crystalline compound analogous to that formed with aldehyde. The compound is separated and purified. When distilled with a solution of sodium carbonate, pure acetone passes over.

Acetone is a colorless liquid having a pleasant, ethereal odor. It boils at  $56.53^\circ$ . It is a good solvent for many carbon compounds. It is used in the manufacture of chloroform, sulphonal, ionone, iodoform, and in gelatinizing nitrocellulose in the manufacture of smokeless powders and celluloid. It is also used as a solvent for acetylene (*Prestolite*), and it is the material from which isoprene, used in the synthesis of rubber, is made. In the laboratory it is much used as a solvent for purifying and recrystallizing organic compounds.

Acetone more closely resembles the aldehydes than any other compounds thus far dealt with. It is not an acid nor an alcohol

as it does not form salts with bases or esters with acids. It is not an ethereal salt, for on boiling with an alkali it does not yield an alcohol and the salt of an acid. On the other hand, it unites with the acid sulphites like the aldehydes. Further, when treated with phosphorus pentachloride its oxygen is replaced by two chlorine atoms thus:—



and, when treated with nascent hydrogen, it is converted into a substance having alcoholic properties. These facts lead to the conclusion that the substance contains carbonyl,  $\text{CO}$ , as the aldehydes do. This is shown in the formula  $\text{C}_2\text{H}_4\text{CO}$ . The formation from calcium acetate leads further to the belief that the group  $\text{C}_2\text{H}_5$  consists of two methyls, as the simplest interpretation of the reaction given above. According to this, acetone is a compound of two methyl groups and carbonyl, or it is carbon monoxide whose two free affinities have been satisfied by two methyl groups. ✓

This view can be tested experimentally. If it is correct, it will be seen that acetone is closely related to acetyl chloride. It is acetyl chloride in which the chlorine has been replaced by methyl:—



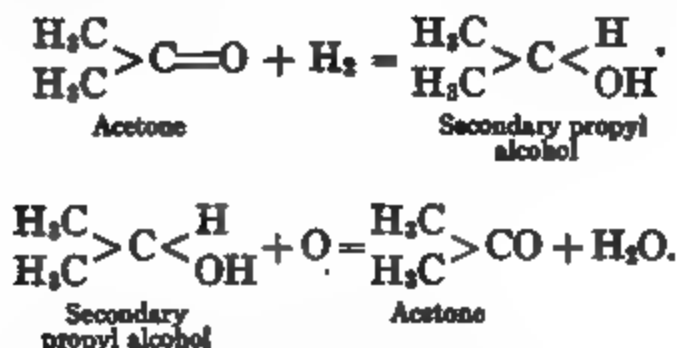
Now, when acetyl chloride is treated with zinc methyl,  $\text{Zn}(\text{CH}_3)_2$ , it yields acetone:—



It will be seen from this that acetone is aldehyde,  $\text{CH}_3\text{CHO}$ , in which the aldehyde hydrogen has been replaced by methyl,  $\text{CH}_3\text{COCH}_3$ .

Like the aldehydes, acetone has the power of taking up other substances, such as the acid sulphites, ammonia, hydrocyanic acid, hydrogen, etc. This power is connected with the relation of the oxygen to the carbon, which is the same in both compounds.

By reduction with nascent hydrogen, acetone yields an alcohol of the formula  $C_3H_8O$ , known as *secondary propyl alcohol*, which when oxidized yields acetone:—



This gives another method for the preparation of ketones, viz. oxidation of the secondary alcohols.

The relation between this alcohol and acetone is the same as that between ethyl alcohol and acetic aldehyde. But while the aldehyde by further oxidation yields acetic acid by simply taking up one atom of oxygen, acetone is decomposed by oxidizing agents, and yields acetic and formic acids:—



Towards oxidizing agents, then, ketones (for it will be shown that other ketones conduct themselves in the same way) act entirely differently from the aldehydes. The alcohol above mentioned as related to acetone is the simplest representative of the secondary alcohols, which differ in some important respects from methyl and ethyl alcohols.

Considerable quantities of acetone are now made by the fermentation of maize (Indian corn) by the Weizmann process.<sup>1</sup> (See Butanol, 133.)

Several mixed ketones, such as methyl ethyl ketone  $\text{CH}_3\text{—CO—CH}_2\text{CH}_3$  (butanone), are also well known. This substance occurs in crude wood alcohol and in crude acetone. In its chemical conduct it resembles acetone very closely. On reduction it gives secondary butyl alcohol and it can be made by

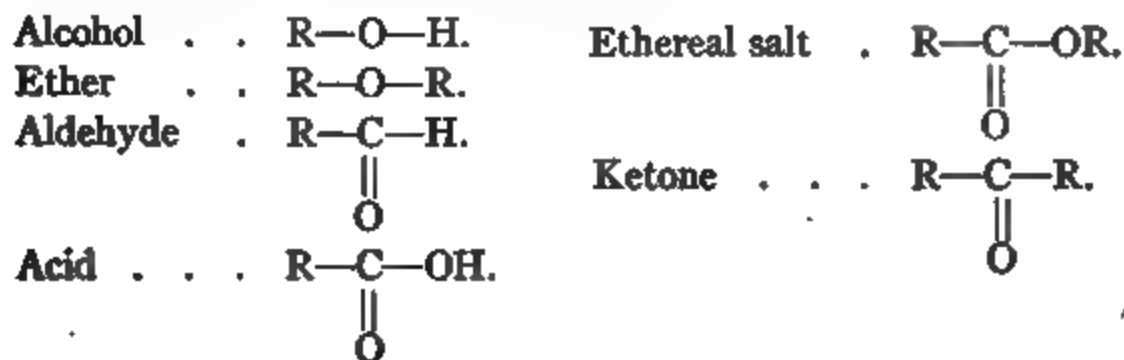
<sup>1</sup>See *Distillation: Principles and Processes*. By Sidney Young (1922), for technical methods of making and distilling acetone.

the oxidation of secondary butyl alcohol. It can also be made by the action of zinc ethyl on acetyl chloride. It is separated from crude acetone by fractional distillation in column stills, and is used in the manufacture of the soporific trional (79). Its presence in crude acetone is due to the fact that the crude calcium acetate used in the manufacture of acetone contains calcium propionate:—



The most important representatives of the six classes of oxygen derivatives of the hydrocarbons have thus far been presented, and, by the aid of a study of their chemical conduct and of the methods used in their preparation, definite views in regard to the relations between them have been formed. In ordinary language these relations may be briefly expressed thus: The alcohols are the hydroxyl derivatives of the hydrocarbons or the hydroxides of certain groups called *radicals*; the ethers are the oxides of these same radicals; the aldehydes are compounds consisting of carbonyl, hydrogen, and a radical; the acids are compounds of carbonyl, hydroxyl, and a radical, or, better, they are carbonic acid in which hydrogen and oxygen, or hydroxyl, have been replaced by a radical; the ethereal salts are compounds like ordinary metallic salts, only they contain a radical in place of the metal; and, finally, the ketones are aldehydes in which the distinctively aldehyde hydrogen has been replaced by a radical, or they are compounds consisting of carbonyl and two radicals.

These ideas are expressed in formulas thus, R being any uni-valent radical like methyl,  $\text{CH}_3$ , or ethyl,  $\text{C}_2\text{H}_5$ :—





## CHAPTER V

### SULPHUR DERIVATIVES OF METHANE AND ETHANE

#### 1. MERCAPTANS

THE simplest derivatives of methane and ethane containing sulphur are the *mercaptans* or *thioalcohols*. They can be made by a method similar to one described under the head of Alcohols. When a monohalogen derivative of a hydrocarbon, as bromomethane,  $\text{CH}_3\text{Br}$ , is heated with the hydroxide of a metal, an alcohol is formed:—

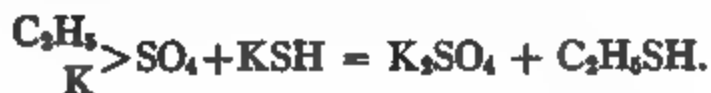


So, also, when a similar halogen derivative is heated with a *hydrosulphide* instead of a *hydroxide*, a compound is obtained that may be regarded as an alcohol in which the oxygen has been replaced by sulphur:—



The compound is called *methylmercaptan* or *methanethiol*.

**Ethyl mercaptan, ethanethiol,  $\text{C}_2\text{H}_5\text{SH}$ .**— This substance can be prepared by heating iodoethane,  $\text{C}_2\text{H}_5\text{I}$ , with an alcoholic solution of potassium hydrosulphide,  $\text{KSH}$ ; also by distilling a mixture of the concentrated solutions of potassium ethylsulphate and potassium hydrosulphide:—

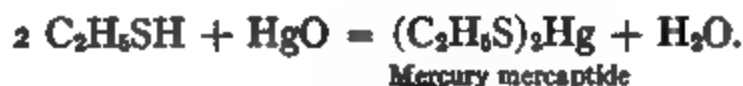


It is a liquid of an *extremely disagreeable odor*; it boils at  $37^\circ$ ; is difficultly soluble in water, and is inflammable. As it is the monoethyl derivative of hydrogen sulphide, it has the character of a weak acid, though having a neutral reaction. It dissolves

in a strong solution of potassium hydroxide to form a mercaptide, analogous to the alcoholate : —

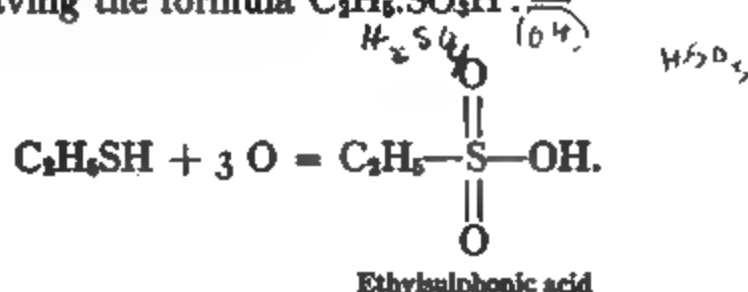


It also reacts, in alcoholic solution, with mercuric oxide : —



For this reason the name *mercaptan* was given to it from *corpus mercurium captans*. It is made on the large scale for the preparation of the soporifics, *sulphonal* and *trional* (78, 79). It forms many other well-characterized metallic derivatives like this mercury compound.

When mercaptan is treated with nitric acid, it is oxidized, the product having the formula  $\text{C}_2\text{H}_5\text{SO}_3\text{H}$  :



This substance is hence a derivative of sulphuric acid.

It will thus be seen that, though in composition mercaptan is analogous to alcohol, towards oxidizing agents it conducts itself quite differently. In the case of alcohol two atoms of hydrogen are replaced by one of oxygen : —



In the case of mercaptan three atoms of oxygen are added directly to the molecule. It will be shown that this new acid, which is called *ethylsulphonic acid*, bears to sulphuric acid a relation similar to that which acetic acid bears to carbonic acid; and that it bears to sulphurous acid a relation similar to that which acetic acid bears to formic acid.

When treated with phosphorus pentachloride it yields a chloride,  $\text{C}_2\text{H}_5\text{SO}_2\text{Cl}$  : —

*Handwritten notes:*  
 $\text{CH}_3\text{CO}$   
 $\text{C}_2\text{H}_5\text{CO}$   
 $\text{HCOO}$

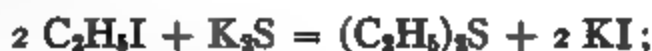


When this is treated with nascent hydrogen (zinc and hydrochloric acid), it is reduced to mercaptan: —

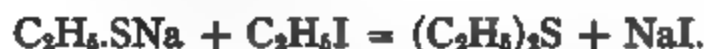


## 2. THIO ETHERS

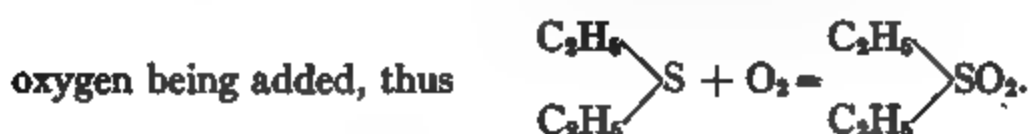
These are compounds similar to the ethers. They contain sulphur in the place of the oxygen of the ethers. Such are methyl sulphide,  $(\text{CH}_3)_2\text{S}$ , and ethyl sulphide,  $(\text{C}_2\text{H}_5)_2\text{S}$ . These are made by treating bromo- or iodomethane or ethane with potassium sulphide: —



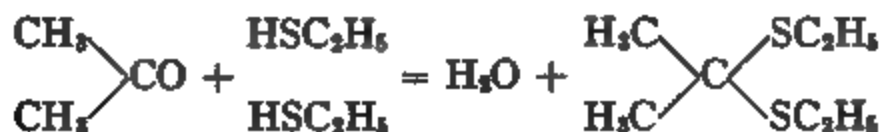
or by treating the sodium salt of methyl or ethyl mercaptan with methyl or ethyl iodide: —



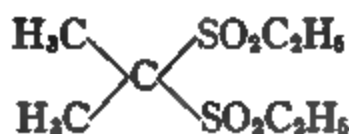
They are liquids with very disagreeable odors. They are present in Ohio petroleum. When oxidized with concentrated nitric acid they are converted into *sulphones*, two atoms of



Acetone reacts with ethyl mercaptan in the presence of hydrochloric acid and gives a thio ether: —



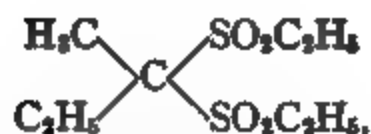
When this ether is oxidized with potassium permanganate, it gives the sulphone: —



This is *sulphonal*, much used as a soporific or hypnotic.

(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S

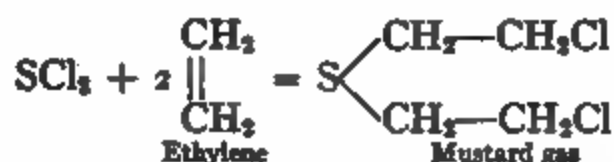
Trional,



which gets its name because it contains three *ethyl* groups, is made in a similar manner from methyl ethyl ketone. It is said to be a better hypnotic than sulphonal.

A derivative of diethyl sulphide that played a very important part in the World War is *mustard gas*. This is a dichlorine sub-

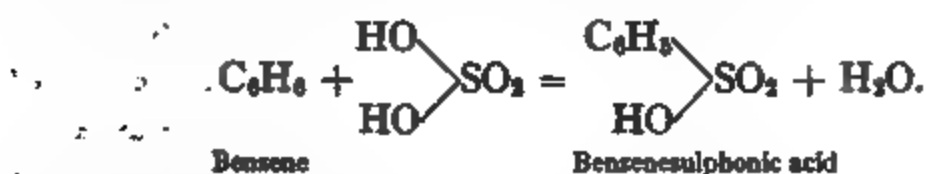
stitution product having the formula  $\begin{array}{c} \text{ClH}_2\text{C}-\text{H}_2\text{C} \\ \quad \quad \quad \diagup \\ \quad \quad \quad \text{S} \\ \quad \quad \quad \diagdown \\ \text{ClH}_2\text{C}-\text{H}_2\text{C} \end{array}$ . It is made by the action of ethylene on sulphur chloride:—



Over 20 tons a day were made in the United States by this method during the war.

### 3. SULPHONIC ACIDS

It was stated above that when mercaptan is oxidized it is converted into an acid of the formula  $\text{C}_2\text{H}_5\text{SO}_3\text{H}$ , or *ethylsulphonic acid*. This is the representative of a large class of substances which are commonly made by treating the aromatic compounds with sulphuric acid. These sulphonic acids can best be studied in connection with the aromatic series of hydrocarbons. Under Benzene it will be shown that when this hydrocarbon is treated with sulphuric acid, a reaction takes place that may be represented thus:—



The sulphonic acid thus obtained can also be made by oxidizing the corresponding phenylmercaptan or hydrosulphide,  $\text{C}_6\text{H}_5\text{SH}$ . Accordingly, the sulphonic acid appears to be sul-

## 80 SULPHUR DERIVATIVES OF METHANE AND ETHANE

phuric acid in which a hydroxyl has been replaced by the phenyl radical,  $C_6H_5$ . We may conclude, therefore that ethylsulphonic acid formed by oxidizing ethylmercaptan bears a similar relation

to sulphuric acid, and corresponds to the formula  $\begin{array}{c} C_2H_5 \\ \diagup \\ SO_2 \\ \diagdown \\ HO \end{array}$

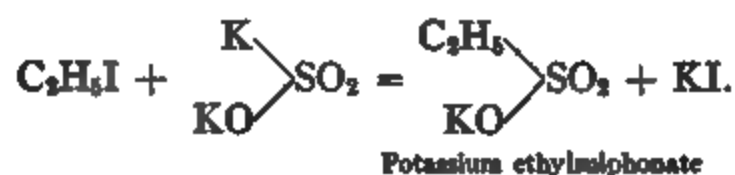
So, also, methylsulphonic acid obtained by oxidation of methyl-

mercaptan should be represented by the formula  $\begin{array}{c} CH_3 \\ \diagup \\ SO_2 \\ \diagdown \\ HO \end{array}$  or

$CH_3.SO_2OH$ . *Its relation to sulphuric acid is the same as that of acetic acid to carbonic acid.* The sulphonic acids are strong monobasic acids, hygroscopic, and readily soluble in water. They are very stable substances and are not saponified by heating with solutions of the caustic alkalies, but form stable salts.

They contain the group  $\begin{array}{c} O \\ \parallel \\ -S \\ \diagdown \\ OH \end{array}$  known as the *sulphoryl* group.

Another method by which the sulphonic acids can be prepared consists in treating a sulphite with a halogen substitution product. Thus ethylsulphonic acid can be prepared from potassium sulphite and iodoethane: —



According to this reaction the sulphonic acids appear to be identical with the acid esters of sulphurous acid, but they are not hydrolyzed like ethereal salts. The sulphonic acids as a class are, for example, much more stable than the ethereal salts as a class. They are closely related to sulphurous acid, and are derived from it by the substitution of a radical for hydrogen, just as acetic acid may be regarded as derived from formic acid by the substitution of a radical for hydrogen. These relations are represented by the following formulas: —

Carbonic acid,	$\text{OC} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$	Sulphuric acid,	$\text{O}_2\text{S} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$
Formic acid,	$\text{OC} \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$	Sulphurous acid,	$\text{O}_2\text{S} \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$
Acetic acid,	$\text{OC} \begin{smallmatrix} \text{CH}_3 \\ \text{OH} \end{smallmatrix}$	Methylsulphonic acid,	$\text{O}_2\text{S} \begin{smallmatrix} \text{CH}_3 \\ \text{OH} \end{smallmatrix}$
Any carboxylic acid,	$\text{OC} \begin{smallmatrix} \text{R} \\ \text{OH} \end{smallmatrix}$	Any sulphonic acid,	$\text{O}_2\text{S} \begin{smallmatrix} \text{R} \\ \text{OH} \end{smallmatrix}$

The difference between a sulphonic acid and an ethereal salt of sulphuric acid should be specially noted. Compare for this purpose ethylsulphuric acid,  $\text{C}_2\text{H}_5\text{O} \begin{smallmatrix} \text{HO} \end{smallmatrix} \text{SO}_2$ , and ethylsulphonic

acid,  $\text{C}_2\text{H}_5 \begin{smallmatrix} \text{HO} \end{smallmatrix} \text{SO}_2$ . Both are monobasic acids, and both contain ethyl, but there is a difference of one atom of oxygen in their composition. The reactions of the substances are such as to lead to the conclusion that in ethylsulphonic acid the ethyl group is directly connected with the sulphur; and that in ethylsulphuric acid the connection is established by means of oxygen. This is shown by the fact that ethylsulphuric acid is readily hydrolyzed even by water alone. It is an ester, whereas ethylsulphonic acid, which is not an ester, cannot be saponified even by boiling with the strongest alkalis. The sulphonic acids are decomposed, however, by fusing with alkalis (see Benzenesulphonic acid (367)).

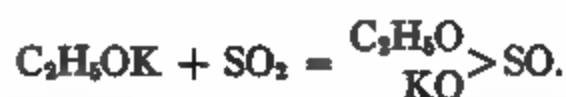
The strongest argument in favor of this view of the structure of the sulphonic acids is perhaps that which is founded on the formation of the sulphonic acids by oxidation of the hydro-sulphides or mercaptans. It can hardly be doubted that in ethyl mercaptan the sulphur is in direct combination with the ethyl; or, to go still farther, that it is in combination

with carbon, as represented in the formula,  $\text{H}_3\text{C} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{S} \text{H}$ .

Now, by oxidation of mercaptan, three atoms of oxygen are added, and the simplest view of the reaction is that the

sulphur is left undisturbed in its relations to ethyl, but that it has taken up the oxygen, as represented in the formula  $\text{C}_2\text{H}_5\text{—SO}_2\text{.OH}$ . As has been shown, the oxygen can be removed again by nascent hydrogen, by reducing the sulphurylchloride, and the result is mercaptan. The study of the sulphonic acids in their relations to sulphuric and sulphurous acids has been of considerable assistance in enabling chemists to form conceptions in regard to the constitution of these two acids. The view which is forced upon us by a consideration of the reactions described above is that sulphurous acid differs from sulphuric acid in containing a hydrogen atom in place of hydroxyl, as represented in the formulas  $\text{O}_2\text{S} < \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$  and  $\text{O}_2\text{S} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ ; and further, that in sulphurous acid one hydrogen is in combination with sulphur and the other with oxygen. According to this the relation is the same as that between carbonic and formic acids.

Potassium ethylsulphonate is isomeric with potassium ethyl sulphite formed by the action of sulphur dioxide on potassium ethylate:—



This salt is very unstable and is hydrolyzed by water:—



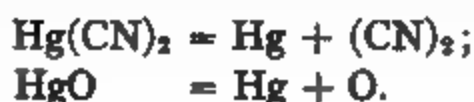
## CHAPTER VI

### NITROGEN DERIVATIVES OF METHANE AND ETHANE

THE simplest compounds of carbon containing nitrogen are hydrocyanic acid and cyanogen. Hydrocyanic acid may be regarded as marsh gas in which three hydrogen atoms have been replaced by one nitrogen, and cyanogen as a similar derivative



**Cyanogen, (CN)<sub>2</sub>.** — Most organic compounds that contain nitrogen give sodium cyanide when heated with sodium. So, also, potassium cyanide is formed when charcoal containing nitrogen is heated with potassium carbonate. Cyanogen itself is readily made by heating mercuric cyanide, Hg(CN)<sub>2</sub>. The decomposition that takes place is, in the main, like the simple decomposition of mercuric oxide in preparing oxygen : —



But, in heating mercuric cyanide, a black solid substance, *para-cyanogen*, is also formed, and remains behind in the retort. It has the same composition as cyanogen, and although its molecular weight is not known, it is a polymeric form of cyanogen, as heat transforms it into cyanogen.

A better method for the preparation of cyanogen is to heat concentrated solutions of potassium cyanide and copper sulphate : —



This reaction is analogous to that which takes place when potassium iodide reacts with copper sulphate, setting iodine



free. Cyanogen thus resembles the halogens. When passed into a solution of potassium hydroxide it reacts very much as chlorine does, forming potassium cyanide and cyanate:—



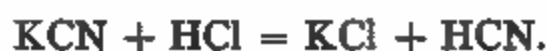
Cyanogen also resembles the halogens in forming an acid with hydrogen, HCN, analogous to the halogen acids, the salts of which resemble those containing the halogens. Thus silver cyanide, precipitated from a solution of potassium cyanide by silver nitrate, is soluble in ammonia and hence resembles silver chloride.

Cyanogen, also called dicyanogen, is present in coal gas and in the blast furnace gases. It boils at  $-20.7^\circ$  and melts at  $-34.4^\circ$ . Water at  $20^\circ$  absorbs 4.5 times, alcohol 23 times, and cocoanut charcoal 1075 times its volume of the gas.

Cyanogen (Gr. *kuanos*, blue) owes its name to the fact that several of its compounds have a blue color. It is a colorless gas, which is readily soluble in water and alcohol, and is *extremely poisonous*. It burns with a purple-bordered flame, giving carbon dioxide and nitrogen.

In aqueous solution, cyanogen soon undergoes change, and a brown amorphous body, azulmic acid, is deposited. The solution then contains hydrocyanic acid, ammonium oxalate, ammonium carbonate, and urea.

**Hydrocyanic acid, prussic acid, HCN.**—This acid is found in many tropical plants; and many plants, especially the phanerogams, contain cyanogen compounds which easily split off hydrocyanic acid, as for example, amygdalin. It is also found in coal gas, and this is the present source of many of the cyanogen compounds. It is prepared by decomposing metallic cyanides with hydrochloric acid, as represented in the equation:—



It can also be made by heating chloroform with alcoholic ammonia and caustic potash:—



It is a volatile liquid, boiling at  $25^{\circ}$ , and melting between  $-10^{\circ}$  and  $-12^{\circ}$ . It has a very characteristic odor, suggesting bitter almonds. It dissolves in water in all proportions, and it is this solution that is known as *prussic acid*. It is one of the weakest acids. Its salts are decomposed by carbon dioxide. Pure hydrocyanic acid is stable, but its aqueous solution decomposes and gives ammonium formate, oxalate, and brown amorphous products. A small quantity of a mineral acid prevents this decomposition. By boiling with alkalis or acids it is converted into formic acid and ammonia. A dilute aqueous solution of hydrocyanic acid is used in medicine. A concentrated aqueous solution of the gas and the gas itself is used to kill insects, parasites, and vermin. It is *extremely poisonous*. It is frequently used in synthetic work, e.g. in the preparation of the hydroxy acids from aldehydes and ketones.

Hydrocyanic acid can be detected by the fact that when its solution is treated with a ferrous and a ferric salt, made alkaline, and heated, a precipitate of Prussian blue is formed when the mixture is acidified; or, by adding yellow ammonium sulphide to its solution, evaporating to dryness, dissolving in water, and then adding a drop of a solution of ferric chloride. If hydrocyanic acid is present, the solution turns a deep blood-red in consequence of the formation of ferric thiocyanate.

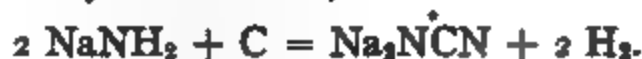
**Cyanides.** — Hydrocyanic, like hydrochloric acid, forms a series of salts, which are called *cyanides*. The cyanides of the alkali metals, of the alkaline earth metals, and mercuric cyanide are soluble in water. The cyanides of the heavy metals have a marked tendency to form double cyanides, and those double cyanides which contain an alkali metal are soluble in water. Hence, the precipitates first formed by potassium cyanide in solutions containing the heavy metals, are dissolved by excess of the cyanide.

**Sodium cyanide, NaCN,** is the most important of all the cyanides on account of its use in extracting gold from low-grade ores, in the manufacture of synthetic indigo, and in gold and silver plating. It has entirely displaced the more expensive potassium salt. It is made on the large scale by heating sodium in an atmosphere

of dry ammonia gas so as to convert it into sodium amide at the lowest possible temperature:—



Carbon is then added and the temperature gradually raised to  $300^\circ$ – $600^\circ$ , when the sodium amide is converted into sodium cyanamide (see Cyanamide 260):—



On raising the temperature to  $700^\circ$ – $800^\circ$  the sodium cyanamide unites with more carbon to form sodium cyanide:—



This method gives a very pure cyanide.

A low-grade sodium cyanide (35–45 per cent) is made by fusing commercial calcium cyanamide (260) with sodium chloride.

Sodium cyanide is *extraordinarily poisonous* and great care should be taken in working with it. It crystallizes out of hot 75 per cent alcohol with two molecules of water of crystallization. It dissolves very readily in water and the solution has an alkaline reaction due to partial hydrolysis:—



When this solution is boiled sodium formate and ammonia are formed:—



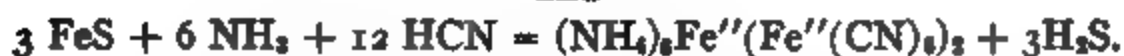
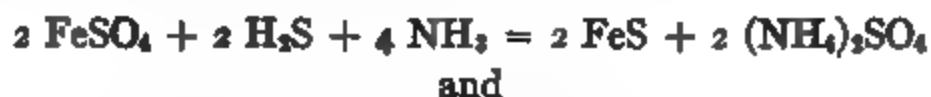
This method is used for the preparation of sodium formate and from it formic acid. The carbon dioxide of the air decomposes sodium cyanide, setting hydrocyanic acid free, and hence the salt has the odor of hydrocyanic acid. In the presence of air sodium cyanide has the power to dissolve gold, and large quantities are now used for the purpose of extracting gold from low-grade ores:—



Sodium cyanide is used in quantitative analysis and also in the preparation of organic compounds, for example in the preparation of veronal (267) and of synthetic indigo.

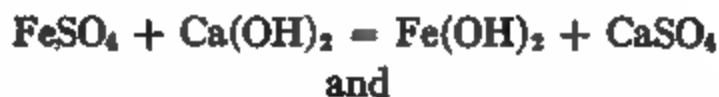
*Ferrous and ferric cyanides*,  $\text{Fe}''(\text{CN})_2$  and  $\text{Fe}'''(\text{CN})_3$ , are unknown. When a solution of potassium cyanide is added to a solution of a ferrous or ferric salt, yellow precipitates are formed which dissolve in excess of potassium cyanide to form double cyanides, potassium ferrocyanide,  $4 \text{ KCN} \cdot \text{Fe}''(\text{CN})_6$ , and potassium ferricyanide,  $3 \text{ KCN} \cdot \text{Fe}'''(\text{CN})_6$ . These compounds are salts of hydroferrocyanic acid,  $\text{H}_4\text{Fe}''(\text{CN})_6$ , and hydroferricyanic acid,  $\text{H}_5\text{Fe}'''(\text{CN})_6$ , and these acids are precipitated when strong solutions of the salts are treated with concentrated hydrochloric acid. The aqueous solutions of the salts of these two acids do not contain any iron ions, or cyanogen ions, but the complex ions, ferrocyanogen,  $\text{Fe}''(\text{CN})_6$ , and ferricyanogen,  $\text{Fe}'''(\text{CN})_6$ . Thus, they are not poisonous and give no precipitate of iron hydroxide with alkalis, nor do they react with silver nitrate to give insoluble silver cyanide as the simple cyanides do.

*Potassium ferrocyanide* and *sodium ferrocyanide* are now manufactured from the hydrocyanic acid present in coal gas or in the gases from the coking ovens. In the Bueb process, iron sulphate and ammonia are used to combine with the hydrocyanic acid, the resulting compound being insoluble ammonium ferrous ferrocyanide:—



The insoluble ammonium ferrous ferrocyanide is heated with lime to recover the ammonia and to give calcium ferrocyanide.

In the Feld process iron sulphate and lime are used to remove the hydrocyanic acid from the gases, the final product being calcium ferrocyanide:—



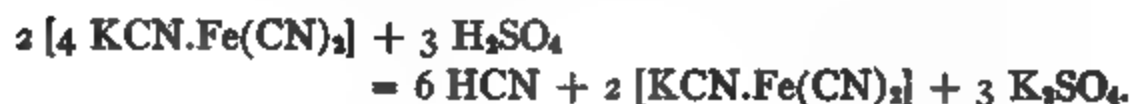
The calcium ferrocyanide is then converted into the potassium or sodium salt by heating the solution with potassium or

sodium carbonate, filtering off the calcium carbonate, and evaporating the solution to crystallization.

**Sodium ferrocyanide**,  $\text{Na}_4\text{Fe}''(\text{CN})_6 + 12\text{H}_2\text{O}$ , crystallizes in yellow monoclinic prisms. It has displaced the potassium salt for most purposes.

**Potassium ferrocyanide**,  $\text{K}_4\text{Fe}''(\text{CN})_6 + 3\text{H}_2\text{O}$ , *yellow prussiate of potash*, crystallizes in large lemon-yellow, monoclinic plates, readily soluble in water but insoluble in alcohol.

When the ferrocyanide is treated with dilute sulphuric acid it yields hydrocyanic acid thus: —



This reaction is the one actually made use of for the preparation of hydrocyanic acid, which is separated from the water by fractional distillation.

When concentrated sulphuric acid is used, the hydrocyanic acid first formed is hydrolyzed to formic acid, which is decomposed by the sulphuric acid into carbon monoxide and water. This method is used in the laboratory for the preparation of carbon monoxide.

**Potassium ferricyanide**,  $\text{K}_3\text{Fe}'''(\text{CN})_6$ . — This salt, known as *red prussiate of potash*, is prepared by treating the ferrocyanide with chlorine or potassium permanganate: —



Potassium ferricyanide is easily soluble in water, and crystallizes from its concentrated solutions in large, dark-red, orthorhombic prisms. It is used in making blue-print paper and as a reagent in the laboratory.

In alkaline solutions it is an excellent oxidizing agent. Reducing agents, such as hydrogen sulphide, sodium thiosulphate (hyposulphite), etc., convert it into the yellow salt.

*Prussian blue*, *Turnbull's blue*, or *Williamson's blue* is precipitated when a solution of potassium or sodium ferrocyanide is

treated with an *excess* of ferric chloride. It is ferric ferrocyanide,  $\text{Fe}_4'''(\text{Fe}''(\text{CN})_6)_3$ . It is used as a blue pigment. *Soluble Prussian blue* is formed when a solution of ferric chloride is treated with an *excess* of potassium or sodium ferrocyanide. It is potassium ferric ferrocyanide,  $\text{KFe}'''(\text{Fe}''(\text{CN})_6)$ .

**Sodium ferricyanide**,  $\text{Na}_3\text{Fe}'''(\text{CN})_6 + \text{H}_2\text{O}$ , crystallizing in ruby red prisms, readily soluble in water, has practically displaced the more expensive potassium salt.

For a full account of the many compounds of the metals and cyanogen, the student is referred to larger works.<sup>1</sup>

**Cyanogen chloride.** — When chlorine is allowed to act upon cyanides or dilute hydrocyanic acid, a volatile liquid is formed which has the composition represented by the formula  $\text{NCCl}$ . It boils at  $12.5^\circ$ , and its vapor acts upon the eyes, causing tears. It is the chloride of cyanic acid. It is known as *liquid cyanogen chloride* to distinguish it from its polymer, *solid cyanogen chloride*. The latter, known as cyanuric chloride, has the formula  $(\text{CN})_3\text{Cl}_3$ , (m. p.  $145^\circ$ ) and is formed by treating anhydrous hydrocyanic acid with chlorine in direct sunlight. The liquid variety is partially transformed into the solid when kept in sealed tubes.

Similar compounds of cyanogen with bromine and iodine are also known.

**Cyanic acid,  $\text{NCOH}$ .** — When a cyanide of an alkali is fused with an oxidizing agent as red lead it takes up oxygen and is converted into a cyanate: —

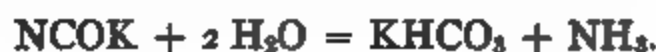


Cyanic acid is readily hydrolyzed by water, yielding ammonium hydrogen carbonate: —



Hence a cyanate effervesces with dilute hydrochloric acid like a carbonate.

The potassium salt is readily soluble in water, but is hydrolyzed when heated with water, yielding ammonia and monopotassium carbonate: —

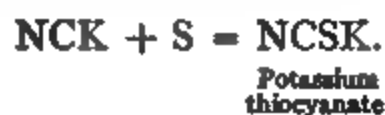


<sup>1</sup> Thorpe's *Dictionary of Applied Chemistry*, article on Cyanides.

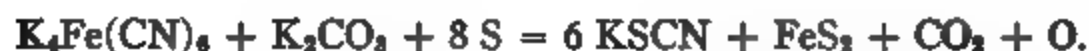
The most interesting salt of cyanic acid is *ammonium cyanate*,  $\text{NCO.NH}_4$ . It can be made by adding ammonium sulphate to a solution of the potassium salt. It is readily soluble in water; but, if allowed to stand in solution, or if its solution is heated to boiling, *it is completely transformed into urea*, which is isomeric with it. The interest connected with this transformation was referred to in the introductory chapter. It will be treated of more fully under urea.

**Cyanuric acid**,  $\text{C}_3\text{N}_3\text{H}_3\text{O}_3 + 2\text{H}_2\text{O}$ . — This acid is a polymer of cyanic acid. It is made by heating cyanuric chloride with water, and also by heating urea. It is a tribasic acid. When distilled it gives cyanic acid.

**Thiocyanic acid**,  $\text{NCSH}$ . — Just as the cyanides of the alkalies take up oxygen and are converted into cyanates, so also they take up sulphur and are converted into thiocyanates: —



**Potassium thiocyanate** is usually made by fusing potassium ferrocyanide with sulphur and potash: —



It crystallizes in long, striated prisms extremely soluble in water. It is deliquescent. When 100 parts of water at  $10.8^\circ$  are mixed with 150 parts of the salt, the temperature sinks to  $-23.7^\circ$ . By evaporation of the solution, the salt can be recovered, as it is not hydrolyzed by water.

**Ammonium thiocyanate**,  $\text{NCS.NH}_4$ . — This salt is most easily prepared by treating carbon bisulphide with concentrated alcoholic ammonia: —



The salt crystallizes in plates. It melts at  $130^\circ$ – $140^\circ$ , and at this temperature is partly transformed into the isomeric substance thiourea (267). (Analogy to transformation of ammonium cyanate into urea.)

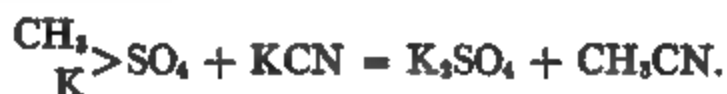
**Ferric thiocyanate**,  $\text{Fe}(\text{SCN})_3$ , is the red compound formed when ferric chloride and potassium or ammonium thiocyanate react. The reaction is used as a test for ferric iron.

Having thus dealt with the more important simpler cyanogen compounds, some of the nitrogen derivatives of the hydrocarbons will now be taken up. These may be divided into three classes:—

- (1) *Those which are related to the cyanides;*
- (2) *Those which are related to ammonia;*
- (3) *Those which are related to nitric acid.*

#### CYANIDES OR NITRILES

**Methyl cyanide, ethane nitrile**,  $\text{CH}_3\text{CN}$ . — This is present in the first runnings obtained in the rectification of crude benzene,  $\text{C}_6\text{H}_6$ . It is formed by distilling potassium methyl sulphate with potassium cyanide:—



It is best made from potassium cyanide and dimethyl sulphate:—



It is a liquid, boiling at  $81.6^\circ$ ; miscible in all proportions with water; it burns with a luminous flame.

According to the method of preparation, it must be regarded as an ethereal salt of hydrocyanic acid, containing methyl in the place of the potassium of the potassium salt.

**Ethyl cyanide, propane nitrile**,  $\text{C}_2\text{H}_5\text{CN}$ . — This is made in the same way as the methyl compound. Also by heating chloroethane with potassium cyanide:—



It is a liquid boiling at  $97.08^\circ$ ; soluble in water; it is just as poisonous as hydrocyanic acid.



The two most characteristic reactions of these cyanides are (1) that which is effected by solutions of caustic alkalies or mineral acids, and (2) that effected by nascent hydrogen.

When methyl cyanide is heated with a solution of caustic potash, it yields potassium acetate and ammonia:—



With dilute mineral acids acetic acid and ammonia are formed:



This reaction is strictly analogous to that which takes place with hydrocyanic acid, yielding formic acid (55). In the same way ethyl cyanide yields propionic acid,  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ . Thus, by making a cyanide, we have it in our power to make an acid containing the same number of carbon atoms.

This reaction, therefore, makes it possible to pass from an alcohol to an acid containing one atom of carbon more than the alcohol contains. It has been of great service in the study of the compounds of carbon.

NOTE FOR STUDENT. — Show how, by starting with methyl alcohol, acetic acid may be made by passing through the cyanide. How is acetic acid converted into methyl alcohol?

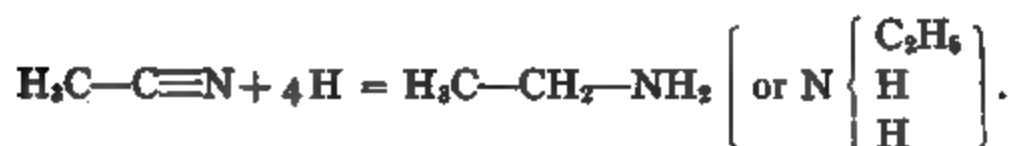
There are two ways in which the cyanogen group can be linked to methyl in methyl cyanide; *viz.*, either by the carbon atom, as represented in the formula,  $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ , or by the nitrogen atom, as represented thus,  $\text{H}_3\text{C}-\text{N}\equiv\text{C}$ . The ease with which the nitrogen is separated from the compound, leaving the two carbon atoms united, as shown in the reaction with caustic potash, naturally leads to the conclusion that the former view is the correct one. If this is correct, it would appear to follow that in potassium cyanide the potassium is in combination with carbon, as represented in the formula  $\text{K}-\text{C}\equiv\text{N}$ , and further that in hydrocyanic acid the hydrogen is in combination with carbon, as shown thus,  $\text{H}-\text{C}\equiv\text{N}$ , since it gives formic acid and ammonia when hydrolyzed.

In consequence of the close relation existing between the cyanides and the acids, the former are often called the *nitriles* of the acids. Thus methyl cyanide, which is converted into acetic acid by boiling with dilute mineral acids, is called the nitrile of acetic acid, or *acetonitrile*, ethane nitrile. In the same way hydrocyanic acid itself may be regarded as the nitrile of formic acid, or *formonitrile*, methane nitrile.

When methyl cyanide is treated with nascent hydrogen, it is converted into a substance which closely resembles ammonia, known as *ethylamine*. It will be shown to bear to

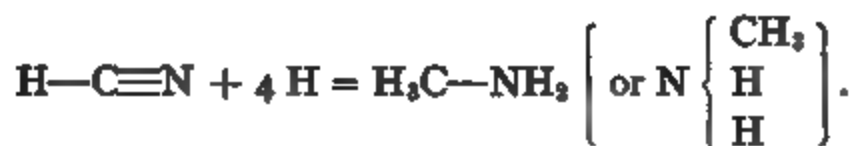
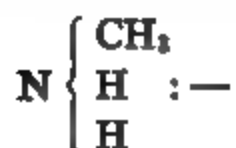
ammonia the relation indicated by the formula  $N \begin{Bmatrix} C_2H_5 \\ H \\ H \end{Bmatrix}$ ; i.e.,

it is ammonia in which one hydrogen has been replaced by ethyl. The reaction may be represented by the equation:—



This transformation strengthens the conclusion already reached, that the two carbon atoms in methyl cyanide are directly united. If this were not the case, it is difficult to see how a compound containing ethyl in which the two carbon atoms are unquestionably united, could be formed so easily from it.

Just as methyl cyanide yields ethylamine when treated with nascent hydrogen, so hydrocyanic acid yields methylamine,



The amines, or substituted ammonias, will be treated of more fully hereafter.

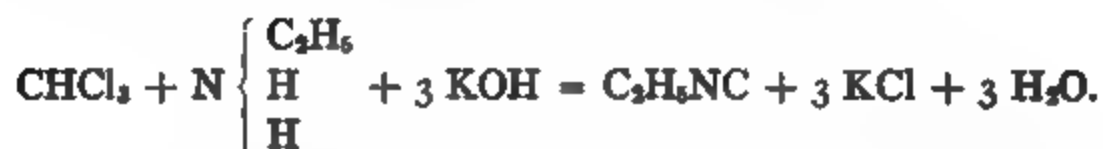
## ISOCYANIDES OR CARBYLAMINES

If, in making an ethereal salt of hydrocyanic acid from a salt, the silver salt is used, a compound is obtained having the same composition as the cyanide, but differing very markedly from it. The substance thus obtained is called an *isocyanide* or *carbylamine*.

**Ethyl isocyanide or ethyl carbylamine,  $C_2H_5NC$ .** — This compound is obtained when silver cyanide and iodoethane are heated together: —



It is also formed when chloroform and ethylamine are heated with potassium hydroxide in alcoholic solution: —

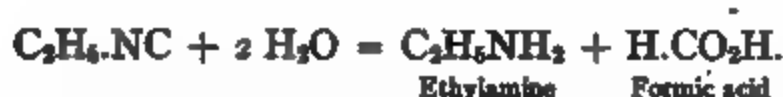


It is a liquid boiling at  $79^\circ$ . It is characterized by an *extremely disagreeable odor*. The methyl compound obtained by the same method boils at  $59.6^\circ$ , but otherwise has properties almost identical with those of ethyl isocyanide.

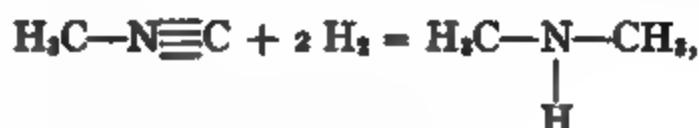
The reactions of these substances are quite different from those of the cyanides. They are decomposed only with great difficulty by the caustic alkalies; but, when heated with dilute hydrochloric acid, they undergo an interesting change, which is represented by the following equation in the case of the methyl compound:



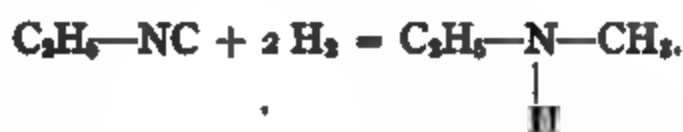
This reaction indicates that in the isocyanides the isocyanogen group is united to the radical by means of nitrogen, as represented by the formula  $H_3C-N\equiv C$ . This is probably the reason why when they undergo hydrolysis, the nitrogen remains in combination with the radical, while the carbon of the isocyanogen group passes out of the compound. The conduct of ethyl isocyanide is represented by the equation: —



The isocyanides are reduced by nascent hydrogen to secondary amines. Thus methyl isocyanide gives dimethylamine:—



while ethyl isocyanide gives ethylmethylaniline:—



These reactions show that the radicals, methyl and ethyl, are in combination with the nitrogen in the isocyanides.

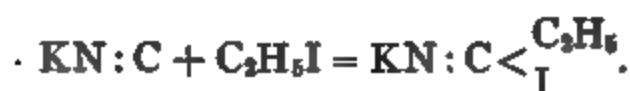
Some chemists assume the presence of bivalent carbon in the isocyanides as in carbon monoxide.

The isocyanides give the isocyanates (96) on oxidation:—

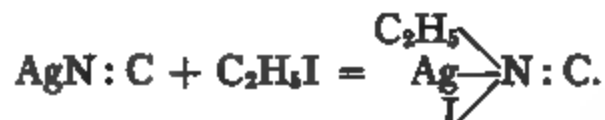


The reactions of the cyanides and of the isocyanides, and the conclusions drawn from them, admirably illustrate the methods used in determining the structure of compounds of carbon; and they are especially valuable, as the connection between the facts and the conclusions, as expressed in the formulas, can be traced so clearly.

The fact that the silver salt of hydrocyanic acid yields isocyanides, while the potassium and other salts yield cyanides, with the halogen derivatives of the hydrocarbons, suggests that in silver cyanide the metal may be in combination with nitrogen and not with carbon, while in the potassium salt it may be in combination with carbon. Another possible view is that the cyanides in general have the constitution  $\text{MN:C}$ , in which M represents a univalent metal. When ethyl iodide acts upon potassium cyanide, the principal reaction is direct addition:—



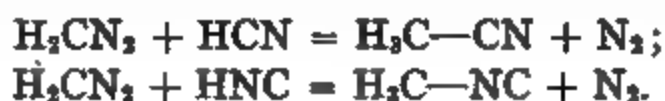
If the product should break down with elimination of potassium iodide, the result would be a cyanide,  $\text{N}\equiv\text{C.C}_2\text{H}_5$ . In the case of silver cyanide the first action may be this:—



The addition product thus formed would then break down into silver iodide and the isocyanide  $\text{C}_2\text{H}_5\text{N:C}$ .

A fact to be borne in mind in connection with the relations between the cyanides and the isocyanides is that it has been shown that some of the isocyanides are transformed into cyanides by heat.

Taking into consideration the facts presented by hydrocyanic acid, the cyanides and isocyanides, it seems not improbable that the acid is capable of assuming both forms represented by the formulas  $\text{HN:C}$  and  $\text{N:CH}$ , and that the salts are derived from one or the other of these forms or both. Phenomena of this kind are not uncommon. Thus diazomethane reacts with hydrocyanic acid and gives both methyl cyanide and methyl isocyanide:—



A compound that reacts as though it had two different formulas is called a *tautomeric* compound. The phenomenon is called *tautomerism*.

#### ISOCYANATES

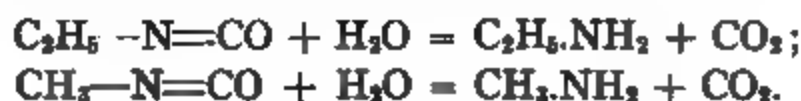
Two series of compounds bearing to cyanic acid the same relation that the cyanides and isocyanides bear to hydrocyanic acid may be expected.

The *cyanates* of the formula  $\text{R—O—CN}$  have not yet been obtained.

In the *isocyanates* (first called *cyanates*) the radical is believed to be united to the nitrogen, as represented thus,

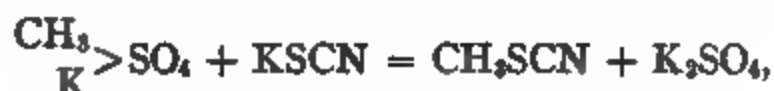
$R-N=CO$ . The isocyanates are made by distilling potassium cyanate with the potassium salt of methyl or ethylsulphuric acid. They can be made also by heating iodoethane or iodoethane with silver cyanate. They are very volatile substances, with penetrating and suffocating odors.

The isocyanates readily yield substituted ammonias on hydrolysis, just as the isocyanides do:—



### THIOCYANATES

The ethereal salts of thiocyanic acid are easily made by distilling potassium thiocyanate and the potassium salt of methyl or ethylsulphuric acid under reduced pressure:—

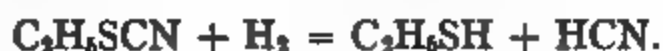


and also by the action of cyanogen chloride on sodium methyl sulphide or sodium ethyl sulphide:—



which shows at once the structure of the compounds. The ethyl compound, which is very similar to the methyl compound, is a liquid boiling at  $142^\circ$ .

When boiled with fuming nitric acid, it is oxidized to ethylsulphonic acid. Now, it has been shown that in ethylsulphonic acid the ethyl is in combination with the sulphur. It hence follows that, in the thiocyanates obtained from potassium thiocyanate, the radical is also in combination with sulphur, as indicated in the formula,  $C_2H_5-S-CN$ . This view is supported by the fact that ethyl thiocyanate readily yields ethyl mercaptan when treated with nascent hydrogen:—

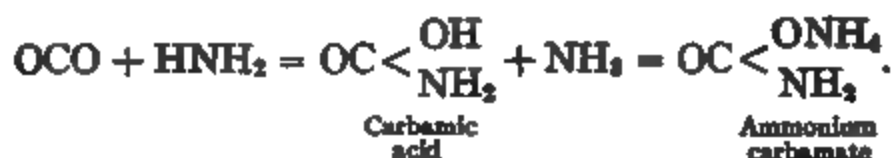


The hydrocyanic acid first formed is reduced to methylamine. The thiocyanates are converted into isothiocyanates or mustard oils by distillation.

## ISOTHIOCYANATES OR MUSTARD OILS

These are compounds isomeric with the thiocyanates. The best-known member of the class is ordinary *mustard oil*, allyl isothiocyanate (283), to the presence of which in *mustard seed*, the peculiar pungent odor and taste of mustard are due. Hence they are generally called *mustard oils*. The mustard oils are made by means of a series of somewhat complicated reactions, which it is rather difficult to interpret without a comparison with some similar reactions that take place between simpler substances.

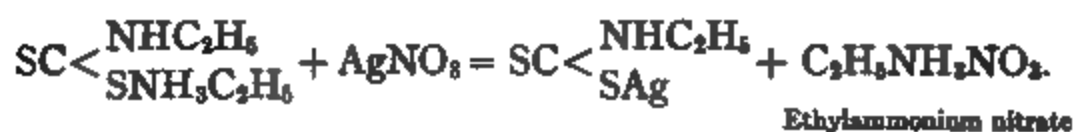
When dry ammonia and dry carbon dioxide act upon each other, so-called anhydrous ammonium carbonate is formed. This is really the ammonium salt of carbamic acid,  $\text{OC} < \begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix}$ . Its formation is represented thus:—



Now, remembering that carbon bisulphide is similar to carbon dioxide, and that ethylamine is similar to ammonia, we can readily understand what takes place when these two substances are brought together:—



The product formed is the ethylammonium salt of the acid  $\text{SC} < \begin{smallmatrix} \text{NHC}_2\text{H}_5 \\ \text{SH} \end{smallmatrix}$ , which is called ethyldithiocarbamic acid. When a solution of this ethylammonium salt is treated with silver nitrate, the corresponding silver salt is precipitated:—



Finally, when this silver salt is boiled with water, it breaks down, yielding *ethyl mustard oil*, silver sulphide, and hydrogen sulphide:—



**Ethyl mustard oil** is an oily liquid that does not mix with water. It has a very penetrating odor, and acts upon the mucous membrane of the eyes and nose in the same way as ordinary mustard oil. Its boiling point is  $134^\circ$ .

Some of the arguments have been stated which lead to the view that in the thiocyanates the radical is in combination with sulphur. The reactions of the mustard oils lead just as clearly to the conclusion that in them the radical is in combination with nitrogen. In the first place, they are made from the amines. Again, when heated with dilute mineral acids, ethyl mustard oil is hydrolyzed, yielding *ethylamine*, carbon dioxide, and hydrogen sulphide:—



And further, nascent hydrogen converts it into *ethylamine* and thioformic aldehyde (*i.e.*, formic aldehyde in which the oxygen has been replaced by sulphur):—



The thioformic aldehyde is at once polymerized to trithioformic aldehyde  $(\text{H}_2\text{CS})_3$ . Thus, the thiocyanates yield mercaptans with nascent hydrogen, while the isothiocyanates yield substituted ammonias. These facts point to the relations expressed in the formulas,  $\text{R}-\text{S}-\text{CN}$  for the thiocyanates, and  $\text{R}-\text{N}=\text{CS}$  for the isothiocyanates or mustard oils.

---

In reviewing now the compounds of the hydrocarbons which are related to cyanogen, it appears that there are two isomeric series of these, the names and general formulas of which are given below:—



Cyanides, $R-C\equiv N$	Isocyanides or Carbylamines,	} $R-NC.$
Cyanates, $R-O-CN$	Isocyanates,	
Thiocyanates, $R-S-CN$	Isothiocyanates or Mustard oils,	} $R-N=CS.$

Of these all are known except the cyanates.

#### SUBSTITUTED AMMONIAS

When methyl iodide is treated with ammonia, methylammonium iodide is formed:—



This reaction is analogous to that which takes place when ammonia and hydriodic acid combine to form ammonium iodide. When methylammonium iodide is distilled with a solution of potassium hydroxide, methylamine is obtained:—



just as ammonia results when ammonium iodide is treated with potassium hydroxide.

Methylamine reacts with methyl iodide just as ammonia does, giving dimethylammonium iodide:—



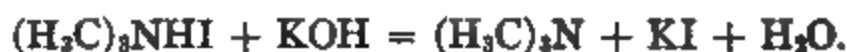
With potassium hydroxide this yields dimethylamine:—



Dimethylamine also reacts with methyl iodide, giving trimethylammonium iodide:—



which with potassium hydroxide gives trimethylamine:—



Finally, the trimethylamine combines with methyl iodide, giving tetramethylammonium iodide:—



The three substances methylamine, dimethylamine, and trimethylamine are regarded as substituted ammonias in which one, two, and three hydrogen atoms of ammonia are replaced by methyl. The last substance is ammonium iodide in which all four hydrogen atoms are replaced by methyl. The names of the substances indicate this relationship.

All the above reactions go on *simultaneously* when ammonia reacts with methyl iodide, the ammonia partly setting free the substituted ammonias from the iodides, and they react at once with the methyl iodide present. It is hence impossible to prepare pure substances by this method. A mixture of the amines is always obtained. It is, however, an excellent method for the preparation of tetramethylammonium iodide.

**Methylamine,  $\text{H}_3\text{CNH}_2$ .** — This compound can be prepared by treating iodomethane with ammonia.

It is best made from dimethyl sulphate and ammonia: —



or by heating formaldehyde (40 per cent solution) with ammonium chloride: —



It was first made by heating methyl isocyanate,  $\text{CH}_3\text{N}=\text{CO}$ , with a solution of caustic potash: —



It has been stated that it is formed by treating hydrocyanic acid with nascent hydrogen: —

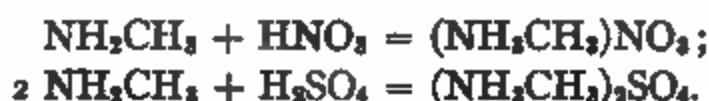


It occurs in nature in herring brine, in *Mercurialis perennis*, and is one of the products of the distillation of nitrogenous animal matter as well as of wood.

Methylamine is a gas that is easily condensed to a liquid. Its boiling point is  $-6^\circ$ . It smells like ammonia and fish. It burns with a yellow flame. It is more strongly basic and more

soluble in water than ammonia, 1 volume of water at 12.5° taking up 1150 volumes of the gas. This solution acts almost exactly like a solution of ammonia in water. Like ammonia it precipitates many metallic hydroxides from solutions of their soluble salts, but, unlike ammonia, it does not dissolve precipitated hydroxides of nickel, cobalt, and cadmium when added in excess. It dissolves aluminium hydroxide.

Methylamine forms salts with acids in the same way that ammonia does; that is, by direct addition. The action towards nitric and sulphuric acids takes place in accordance with the following equations:—



These salts are called methylammonium nitrate and methylammonium sulphate respectively.

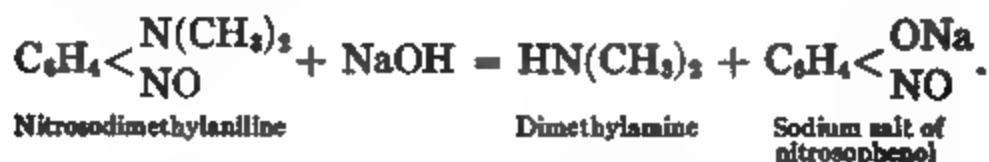
**Dimethylamine,  $\text{NH}(\text{CH}_3)_2$ .**—This is formed by heating iodomethane with alcoholic ammonia:—



and by the action of nascent hydrogen on methyl isocyanide (95).

It is also formed, together with methylamine, as a product of the distillation of wood.

It is best made from nitrosodimethylaniline (346) by heating it with a solution of sodium hydroxide:—



It is a gas which condenses to a liquid at 7.2°. Its properties are much like those of methylamine.

**Trimethylamine,  $\text{N}(\text{CH}_3)_3$ .**—Trimethylamine is formed as one of the products of the treatment of iodomethane with ammonia. It occurs rather widely distributed in nature, as in the blossoms of the English hawthorn, the wild cherry, and the pear. It is contained in large quantity in herring brine, and is a common product of the decomposition by heat of organic

substances that contain nitrogen, like betaine of the sugar beet. It can be obtained from the so-called "vinasse." This is the liquid left after fermenting beet sugar molasses and distilling off the alcohol formed. When it is evaporated to dryness, and the residue subjected to dry distillation, trimethylamine is given off. This is collected as the hydrochloric acid salt,  $N(CH_3)_3HCl$ . When heated with hydrochloric acid, it yields ammonium chloride and chloromethane:—



The chloromethane is utilized for the purpose of producing low temperatures and as a methylating agent.

Trimethylamine is made by heating formalin with ammonium chloride in an autoclave to  $110^\circ$ :—



Trimethylamine is a liquid boiling at  $3.5^\circ$ . It has a strong ammoniacal and fishy odor. It is very soluble in water and alcohol, and is a strong base.

The ethylamines are very much like the methyl compounds, and hence need not be specially described.

When triethylamine is heated with iodoethane, the two unite, forming the compound tetraethylammonium iodide,  $N(C_2H_5)_4I$ , which is to be regarded as ammonium iodide in which all four hydrogen atoms have been replaced by ethyl groups. If silver oxide is added to the aqueous solution of the iodide, silver iodide is formed, and by evaporation of the filtrate crystals of *tetraethylammonium hydroxide*,  $N(C_2H_5)_4OH$ , are obtained. This is plainly the hypothetical ammonium hydroxide in which the four ammonium hydrogens have been replaced by four ethyl groups. *Its solutions act like caustic potash.* It is very caustic, attacks glass, attracts carbon dioxide from the air, saponifies (71) ethereal salts, and gives the same precipitates as caustic potash. It is as strong a base as potassium hydroxide.

*Tetramethylammonium hydroxide*,  $(CH_3)_4NOH$ , is made in the same way as the tetraethyl compound, and is a stronger

base than tetraethylammonium hydroxide. When heated it gives trimethylamine and methyl alcohol:—



Another method for the formation of substituted ammonias in which but one radical is present, as ethylamine,  $\text{NH}_2\cdot\text{C}_2\text{H}_5$ , or in general  $\text{NH}_2\cdot\text{R}$ , consists in treating *nitro compounds* (107) with nascent hydrogen compounds. Nitro compounds are substitution products containing the group  $\text{NO}_2$  in the place of hydrogen. Thus, for example, when nitromethane,  $\text{CH}_3\cdot\text{NO}_2$ , is treated with hydrogen, this reaction takes place:—



In connection with the aromatic compounds, it will be shown that this reaction is a most important one, from an industrial as well as a scientific point of view. It may be said in anticipation that the manufacture of aniline, and consequently of all the many valuable dyestuffs and other compounds derived from and related to aniline, is based upon this reaction.

Just as we may look upon methylamine and the related compounds as ammonia in which one hydrogen atom is replaced by methyl, so also we may regard them, and with equal right, as marsh gas, in which hydrogen has been replaced by the group or residue  $\text{NH}_2$ . Owing to the frequency of the occurrence of this univalent group in carbon compounds, and for the sake of simplifying the nomenclature, it has been called the *amino* group, and the compounds containing it *amino compounds*. Thus the compound  $\text{NH}_2\cdot\text{C}_2\text{H}_5$  may be called either *ethylamine* or *aminoethane*.

Similarly, those substituted ammonias which contain two hydrocarbon residues, as diethylamine,  $\text{NH}(\text{C}_2\text{H}_5)_2$ , are called *imino compounds*, and the bivalent group,  $\text{NH}$ , the *imino* group. Substituted ammonias containing *one* hydrocarbon residue, as ethylamine,  $\text{H}_2\text{NC}_2\text{H}_5$ , are called *primary amines*. Those containing *two* residues, as diethylamine,  $\text{NH}(\text{C}_2\text{H}_5)_2$ , are known as *secondary amines*; and those containing *three* residues, as triethylamine,  $\text{N}(\text{CH}_3)_3$ , are called *tertiary amines*.

Among the most important of the reactions of amino compounds or primary amines is that with nitrous acid. In order to understand what takes place when these compounds are treated with nitrous acid, it is necessary to keep in mind the fact that they are substituted ammonias and hence that their reactions will be similar to those which take place with ammonia itself. Thus with nitrous acid ammonia unites directly to form ammonium nitrite:—



So also ethylamine forms ethylammonium nitrite:—



Ammonium nitrite breaks down readily into free nitrogen and water:—



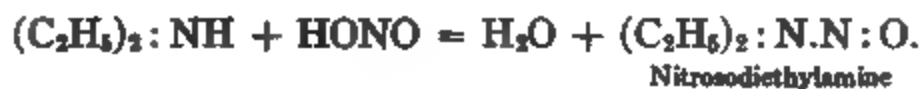
So also ethylammonium nitrite breaks down into free nitrogen, water, and *alcohol*:—



The two reactions are strictly analogous. As in the second case we start with a substituted ammonia, we get as a product a *substituted water* or alcohol.

This reaction has been used extensively in the preparation of compounds containing hydroxyl. For ordinary alcohol it is not a convenient method of preparation; but it will be shown that there are alcohols for the preparation of which it is by far the best method. The essential character of the transformation effected by it will be best understood by comparing the formulas of the amino compound and the alcohol. We have ethylamine,  $\text{C}_2\text{H}_5.\text{NH}_2$ , and from it we get alcohol,  $\text{C}_2\text{H}_5.\text{OH}$ . Thus it will be seen that the transformation consists in replacing the amino group by hydroxyl.

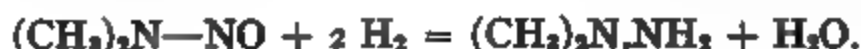
With secondary amines nitrous acid gives nitroso compounds:—



With tertiary amines nitrous acid does not act, or acts as an oxidizing agent. Thus the reactions with nitrous acid enable us to distinguish between a primary, secondary, and tertiary amine. Attention should also be called to the fact that only the primary amines give isocyanides (94) and mustard oils (98), and hence these reactions are also used to distinguish the primary amines from the secondary and tertiary amines.

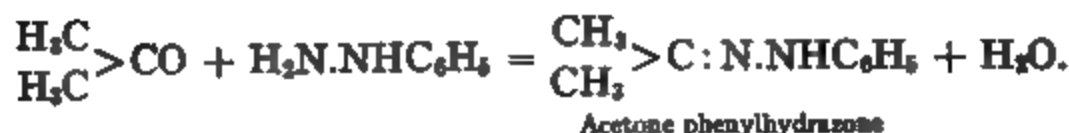
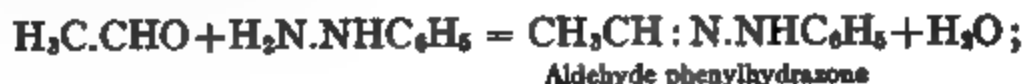
### SUBSTITUTED HYDRAZINES

There is an important class of compounds that bear the same relation to hydrazine,  $\text{H}_2\text{N}-\text{NH}_2$ , that the substituted ammonias bear to ammonia. The reactions by which they are prepared are similar to those used in making the substituted ammonias. Thus methylhydrazine results from the action of methyl iodide on hydrazine, and dimethyl hydrazine,  $(\text{CH}_3)_2\text{N}-\text{NH}_2$ , is formed by reducing nitrosodimethylamine (105):—



The best-known hydrazines are those derived from the hydrocarbons of the benzene series, as, for example, phenylhydrazine,  $\text{C}_6\text{H}_5.\text{NH.NH}_2$  (360).

Phenylhydrazine reacts with aldehydes and ketones, giving phenylhydrazones:—



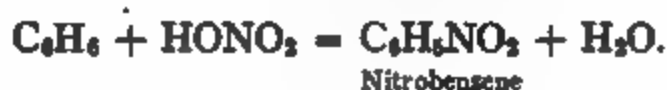
Like the oximes (109) the hydrazones are hydrolyzed by acids:—



The reactions with phenylhydrazine and hydroxylamine (106) are characteristic of the aldehydes and the ketones.

## NITRO COMPOUNDS

Reference has already been made to a class of compounds, containing the group  $\text{NO}_2$ , and known as nitro compounds. They are most readily made by treating the aromatic hydrocarbons with nitric acid. This method, however, is not applicable to the hydrocarbons methane and ethane and their homologues, as these are not readily acted upon by nitric acid. It should be noted, however, that in the presence of aluminium nitrate reaction takes place between the paraffins and nitric acid, and nitro compounds are thus readily made. The hydrocarbon benzene,  $\text{C}_6\text{H}_6$ , is very easily acted upon by nitric acid, when the reaction represented by the following equation takes place:—



The action is like that which takes place between sulphuric acid and benzene, which gives benzenesulphonic acid  $\text{C}_6\text{H}_5\text{SO}_3\text{H}$  (79). In each case a hydroxyl of the acid is replaced by a residue of the hydrocarbon and water is formed. The product in the case of the dibasic acid, sulphuric acid, is itself an acid, while the product in the case of the monobasic nitric acid is not an acid.

The nitro derivatives of methane and ethane have been made by a reaction which we should expect to yield ethereal salts of nitrous acid; namely, by treating iodomethane or -ethane with silver nitrite:—



The compound  $\text{CH}_3\text{NO}_2$ , which is known as *nitromethane*, does not conduct itself like the ethereal salts of nitrous acid. Methyl nitrite,  $\text{CH}_3\text{O.NO}$  (69), can be saponified; nitromethane cannot.

NOTE FOR STUDENT.—Compare the reaction just referred to with that which takes place between silver cyanide and iodomethane; and that which takes place between iodoethane and potassium sulphite. What analogy is there to the former and to the latter?



It has already been stated that the nitro derivatives are converted by nascent hydrogen into the corresponding amino derivatives (104).

NOTE FOR STUDENT.—Write the equations representing the reactions by which methyl alcohol can be converted into methylamine by means of the nitro compound. How is methylamine converted into methyl alcohol?

**Nitroform**,  $\text{CH}(\text{NO}_2)_3$ , as the formula indicates, is trinitromethane. It is converted into *tetranitromethane*,  $\text{C}(\text{NO}_2)_4$ , when treated with a mixture of concentrated sulphuric and fuming nitric acids.

**Nitrochloroform**,  $\text{C}(\text{NO}_2)_2\text{Cl}$ , called also *chloropicrin* and *nitrotrichloromethane*, is formed by distilling methyl or ethyl alcohol with common salt, saltpetre, and sulphuric acid. It is made from picric acid (378) by distilling with bleaching powder, and hence the name. It was used as a "poison gas" in the World War.

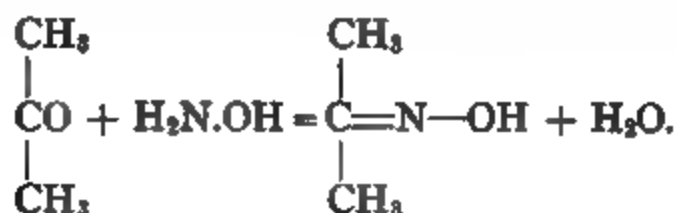
#### NITROSO AND ISONITROSO COMPOUNDS

When a compound containing the group  $\text{CH}$  is treated with nitrous acid, a reaction takes place, which is represented thus:—



The product  $\text{R}_3\text{C.NO}$ , which is derived from the original substance by the substitution of the group  $\text{NO}$  for a hydrogen atom, is called a *nitroso compound*. By oxidation the nitroso compounds are converted into nitro compounds, and by reduction they yield the same products as the corresponding nitro compounds, the primary amines.

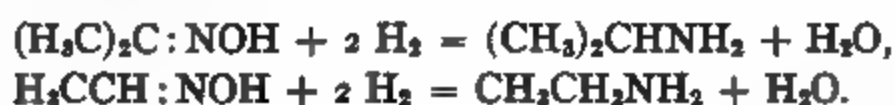
The isonitroso compounds are isomeric with the nitroso compounds. They are formed when ketones or aldehydes are treated with hydroxylamine,  $\text{NH}_2\text{OH}$ . The reaction is represented thus:—



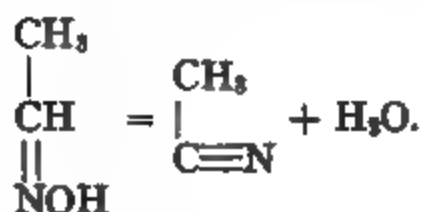
The hydrogen of the hydroxyl has acid properties. The isonitroso compounds are readily hydrolyzed by hydrochloric acid, yielding an aldehyde or ketone and hydroxylamine hydrochloride. They are generally called *oximes*. Those from aldehydes are called *aldoximes*; those from ketones, *ketoximes*.

As hydroxylamine reacts in this way with all aldehydes and with all ketones, it is a valuable reagent for compounds belonging to these classes.

By reduction the oximes are converted into primary amines:—



Aldoximes lose water and give cyanides when heated with acetic anhydride:—



By means of these two reactions acetic aldehyde can be converted into ethylamine or into methyl cyanide by first converting it into the oxime.

**Fulminic acid**,  $\text{CNOH}$ , appears to be an isonitroso compound, and for that reason finds appropriate mention in this place. The principal compound of fulminic acid is the mercuric salt,  $\text{C}_3\text{N}_2\text{O}_2\text{Hg}$ , commonly known as *fulminating mercury*. It is prepared by dissolving mercury in an excess of strong nitric acid, and adding the solution to alcohol. It is extremely explosive. It is used in the manufacture of percussion caps and of cartridges for the explosion of dynamite and guncotton.

When fulminating mercury is treated with concentrated hydrochloric acid, it yields hydroxylamine hydrochloride and formic acid. Fulminic acid is probably the oxime of carbon monoxide, and should be represented by the formula  $\text{C}\equiv\text{N}-\text{OH}$ . As will be seen, fulminic acid is isomeric with cyanic and cyanuric acids (89, 90).

## CHAPTER VII

### DERIVATIVES OF METHANE AND ETHANE CONTAINING PHOSPHORUS, ARSENIC, ETC.

**Phosphorus compounds.** — Corresponding to the amines or substituted ammonias are the substituted phosphines, which, as the name implies, are related to phosphine,  $\text{PH}_3$ . *Methylphosphine*,  $\text{PH}_2\text{CH}_3$ , *dimethylphosphine*,  $\text{PH}(\text{CH}_3)_2$ , and *trimethylphosphine*,  $\text{P}(\text{CH}_3)_3$ , may be taken as examples.

These substances, like the corresponding amines, form salts with acids, though not as readily. The hydroxide, *tetraethylphosphonium hydroxide*,  $\text{P}(\text{C}_2\text{H}_5)_4\text{OH}$ , is a very strong base, though not as strong as the corresponding nitrogen derivative.

The phosphines have one marked property which distinguishes them from the amines, and that is their power to take up oxygen and form acids. Thus, ethylphosphine,  $\text{PH}_2\cdot\text{C}_2\text{H}_5$ , when treated with nitric acid, is converted into *ethylphosphonic acid*,  $\text{PO}(\text{C}_2\text{H}_5)(\text{OH})_2$ , a dibasic acid, bearing to phosphoric acid the same relation that a sulphonic acid bears to sulphuric acid.

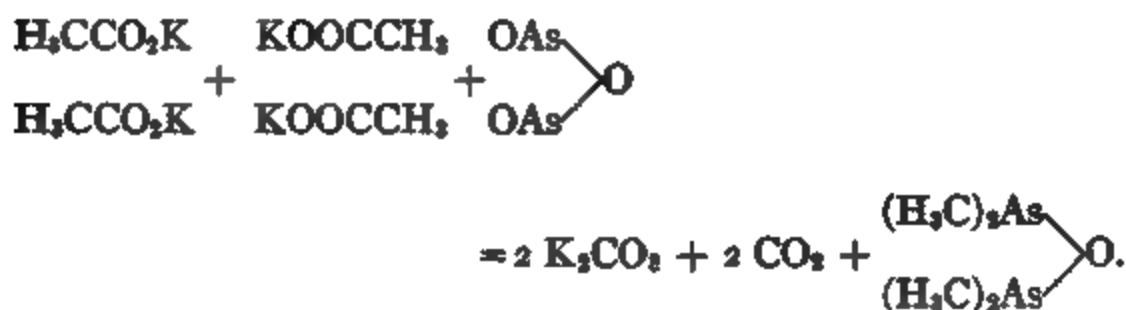
**NOTE FOR STUDENT.** — What is the relation? What other class of acids bears the same relation to carbonic acid? :

Diethylphosphine,  $\text{PH}(\text{C}_2\text{H}_5)_2$ , yields *diethylphosphinic acid*,  $\text{PO}(\text{C}_2\text{H}_5)_2\text{OH}$ , and triethylphosphine gives *triethylphosphine oxide*,  $(\text{C}_2\text{H}_5)_3\text{PO}$ , when oxidized.

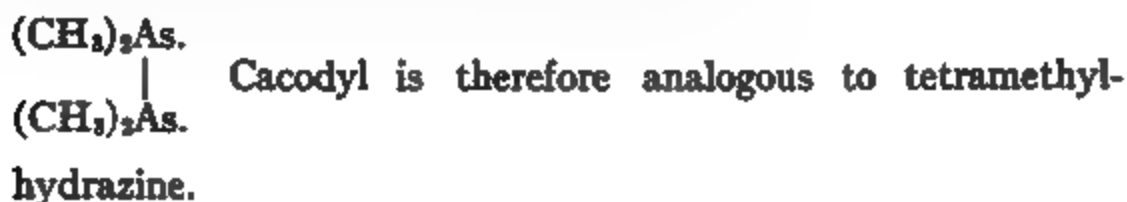
These compounds are not commonly met with, and do not play a very important part in the study of the compounds of carbon.

**Arsenic compounds.** — The most characteristic carbon compound containing arsenic is *cacodyl*, a name given to it on account of its extremely disagreeable odor (Gr. *kakodes*, *stinking*). The oxide is prepared by distilling a mixture of potassium acetate and arsenic trioxide. The reactions that

take place are complicated, and several products are formed. Chief among them is *cacodyl oxide*: —



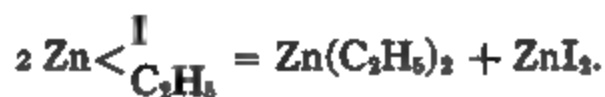
When treated with hydrochloric acid, the oxide is converted into the *chloride*  $(\text{CH}_3)_2\text{AsCl}$ ; and, when the chloride is treated with zinc, cacodyl itself is produced. Its analysis and the determination of its molecular weight lead to the formula  $\text{As}_2\text{C}_4\text{H}_{12}$ , which should be represented thus: —



NOTE FOR STUDENT. — In what does the analogy consist?

It is extremely poisonous and takes fire in the air.

Zinc ethyl,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , is made by treating iodoethane,  $\text{C}_2\text{H}_5\text{I}$ , with zinc alone or with zinc sodium. The reaction takes place in two stages. First, by addition, a compound of the formula  $\text{Zn} < \overset{\text{I}}{\text{C}_2\text{H}_5}$  is formed. When this is distilled, zinc ethyl and zinc iodide are formed: —



It is a liquid boiling at  $118^\circ$ . It takes fire in the air, and burns with a white flame.

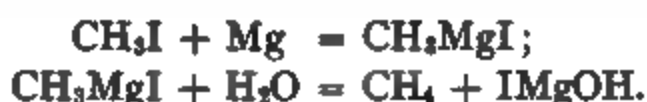
Sodium ethyl,  $\text{C}_2\text{H}_5\text{Na}$ , containing some zinc ethyl, is obtained by treating the latter with sodium. Both these compounds have been used to a considerable extent in the synthesis of

carbon compounds, particularly the more complex hydrocarbons, and they will be frequently referred to in the following pages.

**NOTE FOR STUDENT.** — What is formed when sodium methyl and carbon dioxide are allowed to act upon each other?

Many of the derivatives, like the above, are volatile liquids. Such, for example, are mercury ethyl,  $\text{Hg}(\text{C}_2\text{H}_5)_2$ , aluminium ethyl,  $\text{Al}(\text{C}_2\text{H}_5)_3$ , tin tetraethyl,  $\text{Sn}(\text{C}_2\text{H}_5)_4$ , and silicon tetraethyl,  $\text{Si}(\text{C}_2\text{H}_5)_4$ . The study of these compounds has been of assistance in enabling chemists to determine the atomic weights of some of the elements which do not form volatile inorganic compounds.

**Grignard reaction.** — When magnesium powder is added to a solution of an organic halide, such as methyl iodide, ethyl bromide, etc., in anhydrous ether, magnesium enters into combination with the halide, forming a compound that reacts easily with a variety of substances. The reaction is known by the name of the discoverer, Grignard. A simple example is that indicated below: —



These reactions, as will be seen, afford an easy method of passing from methyl iodide to methane.

### RETROSPECT

In the introductory chapter (17) these words were used in describing the plan to be followed: "Of the first series of hydrocarbons *two* members will be treated. Then the derivatives of these two will be taken up. These derivatives will serve admirably as representatives of the corresponding derivatives of other hydrocarbons of the same series and of other series. Their characteristics and their relations to the hydrocarbons will be dwelt upon, as well as their relations to one another. Thus by a comparatively close study of two hydrocarbons and their derivatives, we may acquire a knowledge of

the principal classes of the compounds of carbon. After these typical derivatives have been discussed, the entire series of hydrocarbons will be taken up *briefly*, only such facts being dealt with at all fully as are not illustrated by the first two members."

In accordance with the plan thus sketched we have thus far studied the principal derivatives of the two hydrocarbons, methane and ethane, so far as these derivatives represent distinct classes of compounds. These derivatives were classified first into: (1) those containing halogens; (2) those containing oxygen; (3) those containing sulphur; and (4) those containing nitrogen. On examining each of these classes more closely, we found that the halogen derivatives, such as chloromethane, bromoethane, etc., bear very simple relations to one another. We found that under the head of oxygen derivatives, the most important and most distinctly characteristic derivatives of hydrocarbons are met with; as, the *alcohols*, *ethers*, *aldehydes*, *acids*, *ethereal salts*, and *ketones*. The sulphur derivatives, some of which closely resemble the oxygen derivatives, include the *sulphur alcohols* or *mercaptans*, *thioethers*, and *sulphonic acids*.

On beginning the treatment of the nitrogen derivatives it was found to be desirable first to take up certain derivatives containing the cyanogen group, among which are cyanogen, hydrocyanic acid, cyanic acid, and thiocyanic acid. Many interesting carbon compounds are closely related to these fundamental compounds. Such, for example, are the *cyanides* and *isocyanides*, the *isocyanates*, the *thiocyanates*, and *isothiocyanates* or *mustard oils*. Following the compounds related to cyanogen, the interesting compounds related to ammonia, the *substituted ammonias* or *amines*, were taken up. Then came the *nitro derivatives*; and, finally, the compounds of the hydrocarbon radicals with metals.

It is of the greatest importance that the student should master the preceding portion of this book. If he studies carefully the reactions that have been presented, which are statements in chemical language that tell us the conduct of the

various classes of derivatives, and if he performs the experiments in the laboratory manual, he will have a general knowledge of the kinds of relations that are met with in connection with the compounds of carbon throughout the whole field. As stated in the Introduction: "If we know what derivatives one hydrocarbon can yield, we know what derivatives we may expect to find in the case of every other hydrocarbon."

The more the student practices the use of the equations thus far given, the better he will be prepared to follow the remaining portions of the book. Indeed, it may be said that, if he thoroughly understands what has gone before, what follows will appear simple. Whereas, if he has failed at any point to catch the meaning, if he has failed to see the connection, he had better go back and review faithfully or he will soon find his mind hopelessly muddled, and relations which are as clear as day will be concealed from him.

An excellent practice is to trace connections between the different classes of compounds, and show how to pass from one to the other. Thus, for example: (1) Show by what reactions it is possible to pass from marsh gas to acetic acid; and from acetic acid to marsh gas. (2) How can we pass from ordinary alcohol to ethylidene chloride,  $\text{CH}_3\text{CHCl}_2$ , and from ethylidene chloride back to alcohol? (3) What reactions enable us to make methylamine from its elements? (4) How can acetone be made from methylamine, and methylamine from acetone? (5) What reactions are necessary in order to make ordinary ether from ethylamine and ethylamine from ether? etc., etc. It is well in this sort of practice to select what appear to be the least closely related compounds, and to show how it is possible to pass from one to the other. Be sure to select representatives of all the classes hitherto mentioned, and to bring in all the important reactions.

## CHAPTER VIII

### THE HYDROCARBONS OF THE MARSH GAS SERIES, OR PARAFFINS

THE existence of the homologous series of hydrocarbons beginning with methane and ethane was mentioned before its first two members were discussed. The extent of the series, and the names and formulas of the more important members of the series, together with their melting points and boiling points, are shown in the table on the following page.

The explanation of the remarkable relation in composition existing between these members, a relation to which the name *homology* is given, has already been given (21). The number of hydrogen atoms contained in a member of this series bears a constant relation to the number of carbon atoms, as expressed in the general formula  $C_nH_{2n+2}$ . On examining the column headed "Boiling point" it will be seen that, as we pass upward in the series, the boiling point becomes higher and higher. The first four members are gases at ordinary temperatures, while nonadecane,  $C_{19}H_{40}$ , boils at  $330^\circ$ . The elevation in the boiling point is to some extent regular, as will be observed. The difference between butane,  $C_4H_{10}$ , and pentane,  $C_5H_{12}$ , is  $36.4 - (-0.3) = 36.7^\circ$ ; that between pentane and the next member is  $69 - 36.4 = 32.6^\circ$ ; between hexane and heptane it is  $98.4 - 69 = 29.4^\circ$ ; between heptane and octane,  $125.5 - 98.4 = 27.1^\circ$ ; and finally, between octane and nonane the difference is  $150.5 - 125.5 = 25^\circ$ . Thus it will be seen that the elevation in boiling point caused by the addition of  $CH_2$  decreases as we pass upward in the series.

The chief natural source of the paraffins is Pennsylvania petroleum; but although this substance, which occurs in such enormous quantities in nature, consists largely of the



## MARSH GAS HYDROCARBONS

PARAFFINS.—HYDROCARBONS,  $C_nH_{2n+2}$ 

FORMULA	NAME	MELTING POINT	BOILING POINT
$CH_4$	Methane	-184°	-164° (760)
$C_2H_6$	Ethane	-172.1	-84.1 (749)
$C_3H_8$	Propane	-187.8	-44.5 (757)
$C_4H_{10}$	Butane	-135	-0.3 (760)
$C_5H_{12}$	Pentane	-147.5	36.4 (760)
$C_6H_{14}$	Hexane	-94	69 (760)
$C_7H_{16}$	Heptane	-97.1	98.4
$C_8H_{18}$	Octane	-56.6	125.5
$C_9H_{20}$	Nonane	-51	150.5 (759)
$C_{10}H_{22}$	Decane	-32	173
$C_{11}H_{24}$	Undecane	-25.6	194.5
$C_{12}H_{26}$	Dodecane	-12	215
$C_{13}H_{28}$	Tridecane	-6.2	234
$C_{14}H_{30}$	Tetradecane	5.5	252
$C_{15}H_{32}$	Pentadecane	10	270
$C_{16}H_{34}$	Hexadecane	18.3	287.5
$C_{17}H_{36}$	Heptadecane	22.5	303
$C_{18}H_{38}$	Octadecane	28	317
$C_{19}H_{40}$	Nonadecane	32	330
$C_{20}H_{42}$	Eicosane	37	205 <sup>1</sup>
$C_{21}H_{44}$	Heneicosane	40	215 <sup>1</sup>
$C_{22}H_{46}$	Docosane	44.4	317.4
$C_{23}H_{48}$	Tricosane	47.7	320.7
$C_{24}H_{50}$	Tetracosane	50.7	324.1
$C_{26}H_{54}$	Hexacosane	58	.
$C_{27}H_{56}$	Heptacosane	60	270 <sup>1</sup>
$C_{31}H_{64}$	Hentriacontane	70	302 <sup>1</sup>
$C_{32}H_{66}$	Dotriacontane	70	310 <sup>1</sup>
$C_{36}H_{74}$	Pentatriacontane	75	331 <sup>1</sup>
$C_{40}H_{82}$	Hexacontane	102	.

members of the paraffin series, it is extremely difficult to isolate them from the mixture. Prolonged fractional distillation is not sufficient. If, however, some of the purest products that can thus be obtained are treated with concentrated sulphuric acid, and afterwards with concentrated nitric and sulphuric acids, and then washed with water and alkali, dried and re-distilled, they can be obtained in approximately pure condition.

<sup>1</sup> These boiling points are taken at 15<sup>mm</sup> pressure.

**Petroleum**<sup>1</sup> or **rock oil** is an oily liquid, occurring in nature, varying in color from a light yellow to a dark red or even black and in many cases having a greenish fluorescence. Some specimens of petroleum are light mobile fluids, while others are heavier and more viscous and some are semisolid. They are all lighter than water, ranging in specific gravity from 0.85 to 0.94. Heavy Mexican crude has nearly the same specific gravity as water. The world's production of petroleum in 1920 was 694,854,000 barrels (of 42 gallons), of which the United States produced 63.8 per cent (443,402,000 barrels valued at \$1,360,000,000), Russia, 3.6 per cent (25,429,600 barrels), and Mexico, 23.5 per cent (163,540,000 barrels). The value of the products manufactured from petroleum in the United States in 1914 was \$396,361,405. California produces more petroleum at the present time than any other state in the Union, 105,668,000 barrels in 1920. Texas produced 96,000,000 barrels.

Petroleum is an exceedingly complicated mixture of *hydrocarbons* usually containing compounds of nitrogen and sulphur, though the amounts of these are generally small. Pennsylvania petroleum consists very largely of the *saturated paraffin hydrocarbons*,  $C_nH_{2n+2}$ , and the members from  $CH_4$  to  $C_{36}H_{74}$  have been isolated from it. *Olefines*,  $C_nH_{2n}$  (275), have been found in Canadian petroleum, but they are usually present in small amount in most petroleums. Russian, Japanese, California, and Texas coastal petroleums consist very largely of *naphthenes*, which are *saturated hydrocarbons*,  $C_nH_{2n}$ , isomeric with the olefines, but having a closed chain structure. Hydrocarbons of the benzene series,  $C_nH_{2n-6}$ , also occur in all petroleums, but in small amounts. *Pyridine* and *quinoline* derivatives have been found in California petroleum, and in some cases they constitute 10 to 20 per cent of the crude product. *Sulphides* from methyl sulphide to hexyl sulphide have been isolated from Ohio petroleum, and cyclic sulphur compounds,  $C_nH_{2n}S$ , occur in Canadian petroleum.

It is generally believed that petroleum has originated from the

<sup>1</sup> See *The American Petroleum Industry*, by R. F. Bacon and W. A. Hamor. 1916.

decomposition of animal and vegetable remains (fats) beneath the earth's surface by the action of heat and pressure.<sup>1</sup>

*Refining of petroleum.*—The American petroleum is divided by the refiners into "Paraffin base," "Asphalt base," and "Mixed base" crudes, as the methods of refining these petroleum are different. Though this is the accepted classification, it seems best to include a fourth class, "Naphthenic base." Many Texas petroleum contain neither asphalt nor paraffin, but, as already stated, consist largely of naphthenes. The petroleum from Pennsylvania, New York, West Virginia, Ohio, Kentucky, northern Louisiana, and Canada contain paraffin wax; those from California and some from Texas, asphalt; while those from Illinois, Kansas, Oklahoma, northern Texas, and Mexico contain both paraffin wax and asphalt. The refining of petroleum consists in separating it into commercial products, such as gasolene, naphtha, lamp oils (kerosenes), gas oils, fuel oils, spindle oils, cylinder oils, paraffin wax, petrolatum (vaseline), dust-laying oils, road binders, and coke.<sup>2</sup> The petroleum is first subjected to distillation. If the refiner desires to produce the maximum amount of gasolene and lamp oil (kerosene) he uses what is called "Cracking Distillation," which means the breaking down of the higher-boiling, heavier fractions by destructive distillation into lighter and more volatile ones. To supplement the cracking that occurs normally in the distillation of crude petroleum, extensive use is now made of distillation in pressure stills in which the distillation is carried on under pressure. If, on the other hand, he wishes to produce the maximum yield of the heavy lubricating oils and petroleum asphalt he uses fractional distillation, injecting dry steam into the petroleum while it is being heated in order to minimize the decomposition of the petroleum by heat and separate it into the fractions which compose it.

*Cracking distillation of mid-continent petroleum.*<sup>3</sup>—When the temperature of the petroleum in the still reaches 175 to 200° F. some gases, largely butane and pentane, are given off and soon the lightest naphtha begins to distil over. The temperature in the still becomes gradually higher until it reaches about 325° F., when about 6 to 8 per cent of crude naphtha (200° F. boiling point) has distilled over. This is set aside and the distillation continued until the temperature in the still has reached about 475° F. This distillate is called crude heavy naphtha. It represents 13 to 15 per cent of the petroleum and has an average boiling point of about

<sup>1</sup> For theories on the origin of petroleum see *The American Petroleum Industry*, Vol. I, p. 13.

<sup>2</sup> For definitions of these terms and others used in the petroleum industry see *The American Petroleum Industry*, Vol. II, p. 845.

<sup>3</sup> Based on a description by the late F. C. Robinson, chief chemist, Atlantic Refining Co. Philadelphia, Pa.

300° F. The distillation is then continued until the temperature in the still has reached about 625° F. for natural lamp oil, which represents about 16 to 18 per cent of the petroleum and has an average boiling point of about 450° F. When the still has reached this temperature "cracking," or destructive distillation, sets in. The fires are slackened in order to distil very slowly, and this slow distillation is continued until the temperature in the still reaches 675 to 700° F., producing a distillate with an average boiling point of about 550° F., but containing some gasolene, some lamp oil, and much heavier oil called gas and fuel oil stock. The yield of this oil is about 20 per cent. In this distillation heavy molecules are broken down into lighter ones by subjecting them to temperatures at which they are unstable. There remains in the still a heavy black tar, representing about 42 per cent of the petroleum. This is the source of paraffin wax and the paraffin lubricating oils. This tar is distilled very rapidly in order to avoid cracking as much as possible and to produce the maximum yield of paraffin distillate (about 22 per cent). In addition to this there is also produced about 15 per cent of cracked distillate. At the end of the distillation the stream becomes so heavy that it will sink in water and is then known as wax tailings, which amounts to about one per cent of the petroleum. When the distillation stops, there remains in the still nothing but coke, amounting to about 4 per cent of the petroleum.

The crude naphtha is distilled usually by injecting live steam into it, for the purpose of separating it into the various gasolenes and naphthas that compose it and also to separate it from the small amount of lamp oil that it contains. The crude heavy naphtha is distilled with steam with the aid of external heat. It contains little or no gasolene, but about 50 per cent of lamp oil. The cracked distillate is also distilled with steam to remove about 4 per cent of crude naphtha. In practice the naphtha and lamp oil distillates are agitated with about one per cent by volume of sulphuric acid for half an hour. The compounds that give color and odor to the distillate combine with the acid, producing a heavy black viscous mass called acid sludge which settles to the bottom of the vessel. The sludge is drawn off and the oil washed with water and alkali to remove all traces of acid and is then ready for the market.

The paraffin distillate is cooled to 20 to 30° F., causing the paraffin wax (amounting to about 10 per cent of the distillate) to solidify. This is removed from the liquid oil by means of a filter press and decolorized by filtering it while hot through fuller's earth. Light lubricating oils are made from the filtrate from the cold filter presses.

In the case of the refining of the light colored, non-asphaltic crude oils from which the valuable cylinder oils are made, live steam is injected into the oil when the temperature is well above the boiling point of water

in order to avoid destructive distillation and to produce the maximum yield of heavy lubricating oils. The effect of this current of steam through the oil is to distil the oil at a temperature below its boiling point, and to allow a heavy oil to be distilled below the temperature of destructive distillation. The crude naphtha is first distilled off as described above, but the temperature only reaches  $280^{\circ}\text{F.}$ , while without steam the temperature was about  $375^{\circ}\text{F.}$  The heating is continued, more and more steam being injected, until the crude heavy naphtha has distilled off. At this point the temperature has reached about  $330^{\circ}\text{F.}$  while without steam it was  $475^{\circ}\text{F.}$  The distillation is continued until the natural lamp oil has distilled off. At this point the temperature in the still is only  $500^{\circ}\text{F.}$  while without steam it was  $630^{\circ}\text{F.}$  The distillation is now carried on as rapidly as possible, more and more steam being admitted to avoid cracking, until the lubricating oil distillate has passed over. The temperature in the still is now about  $620^{\circ}\text{F.}$  The distillation is now stopped, leaving the cylinder oil stock in the still. The various fractions are then put through the same processes as the corresponding fractions from the cracking distillation. It should be stated that large quantities of gasolene are now obtained also from (1) the gases from petroleum wells, (2) from natural gas, and (3) from the cracking of petroleum in pressure stills.

**Synthesis of the paraffins.** — Although the paraffins occur in nature, and can be obtained in pure condition from natural sources, we are dependent upon synthetical operations performed in the laboratory for our knowledge of the series and the relations existing between them.

It has already been shown how ethane can be prepared from methane by treating methyl iodide with sodium, as represented in this equation: —



This method has been extensively used in building up higher members of the series. Thus from ethyl alcohol we can make ethyl iodide, and by treating this with sodium get butane,  $\text{C}_4\text{H}_{10}$ : —

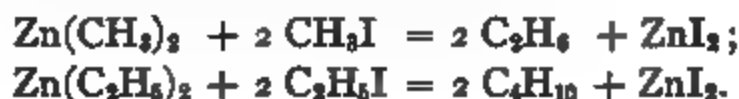


We can get the intermediate member, propane,  $\text{C}_3\text{H}_8$ , by mixing methyl iodide and ethyl iodide and treating the mixture with sodium: —

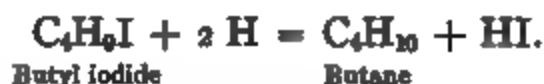


A large number of the members of the paraffin series have been made by this method.

Another method consists in treating the zinc compounds of the radicals, like zinc ethyl,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , with the iodides of radicals. Thus zinc methyl and methyl iodide give ethane; zinc ethyl and ethyl iodide give butane, etc.: —



Paraffins can also be made by replacing the halogen in a substitution product by hydrogen. This can be effected by nascent hydrogen: —



As these halogen substitution products can easily be made from the alcohols, it follows that the hydrocarbons can be made from the corresponding alcohols.

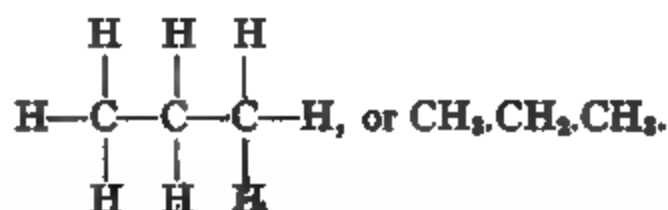
The Grignard reaction can also be used for the purpose of passing from a monohalogen substitution product of a paraffin to the paraffin itself (112).

**Isomerism among the paraffins.** — It has already been stated that the evidence is strongly in favor of the view that each of the four hydrogen atoms of marsh gas bears the same relation to the carbon, and therefore that, as regards the nature of the product, it makes no difference which hydrogen atom is replaced by a given atom or radical. According to this, as ethane is the methyl derivative of marsh gas, it makes no difference which of the hydrogen atoms of marsh gas is replaced by the methyl, the product must always be the same, or *there is only one ethane possible according to the theory, and only one ethane has ever been*

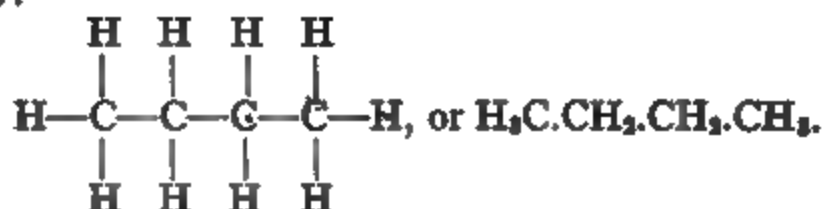
*made.* This is represented by the formula, 
$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$

or  $\text{H}_3\text{C}-\text{CH}_3$ . In ethane, as well as in methane, all the hydrogen atoms bear the same relation to the molecule, and it

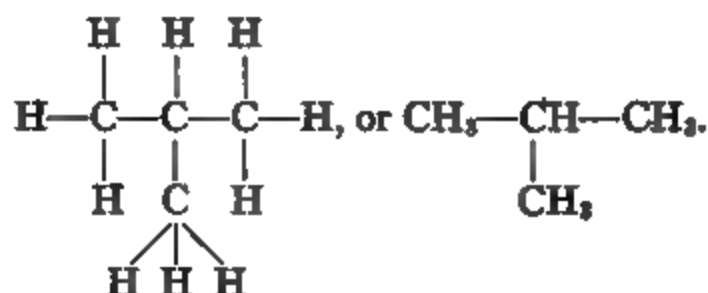
should make no difference which one is replaced by methyl. But propane is regarded as derived from ethane by the substitution of methyl for hydrogen; and, as it makes no difference which hydrogen is replaced, *there is but one propane possible*. Only one has ever been made, and this must be represented thus:—



Now, continuing the substitution of methyl for hydrogen, the theory indicates the possibility of the existence of two compounds of the formula  $\text{C}_4\text{H}_{10}$ . One of these should be obtained by substituting methyl for one of the three hydrogens of either methyl group of propane. It is represented by the formula:—



The other should be obtained by substituting methyl for one of the two hydrogens of the group  $\text{CH}_2$  contained in propane. This would give a hydrocarbon of the formula:—



The theory then indicates the existence of two butanes. How about the facts? Two, and only two, butanes have been discovered. The first has been made synthetically by treating ethyl iodide with zinc:—



The method of synthesis clearly shows which of the two possible isomers the product is. It is known as **normal butane**. It is a gas that can be condensed to a liquid boiling at  $-1^{\circ}$ .

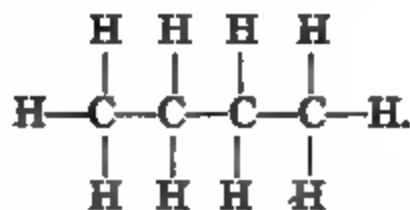
The second, or **isobutane** (2-methylpropane), is made from an alcohol which will be shown to have the structure represented

by the formula  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$  (see Tertiary butyl alcohol,

134), by replacing the hydroxyl by hydrogen. It is a gas which when liquefied boils at  $-11.5^{\circ}$ .

*Cymogene*, a petroleum distillation product, sp. gr. 0.59–0.636 and boiling at  $0^{\circ}$ , is nearly pure butane. Isobutane also occurs in American petroleum.

Applying the same method of reasoning to the next members of the series, how many isomeric varieties of pentane,  $\text{C}_5\text{H}_{12}$ , does the theory suggest? The question resolves itself into a determination of the number of kinds of hydrogen atoms contained in the two butanes, or the number of relations to the molecule represented among the hydrogen atoms of the butanes. This determination can be made best by examining the structural formulas. Take first normal butane:—



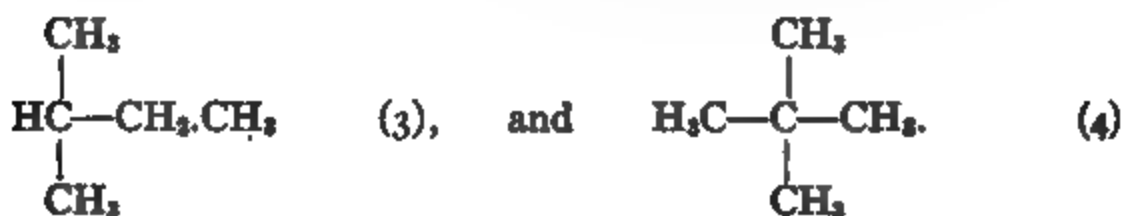
In this there are plainly two different relations represented; viz., that of each of the six hydrogens in the two methyl groups, and that of each of the four hydrogens of the two  $\text{CH}_2$  groups. The two possible methyl derivatives of a hydrocarbon of this formula are therefore to be represented thus:—





Now, taking isobutane,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{HC}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ , it will be seen that it con-

sists of three methyl groups, giving nine hydrogen atoms of the same kind, and one CH group, the hydrogen of which bears a different relation to the molecule from that which the other nine do. There are therefore two possible methyl derivatives of isobutane which must be represented thus:—



Apparently four pentanes are possible. But on comparing formulas (2) and (3), it will be seen that, though written a little differently, they really represent the same compound. Thus the number of pentanes, the existence of which is indicated by the theory, is three, and these are represented by formulas (1), (2), and (4). *They are all known.* The first is called **normal pentane**, boiling point  $36.3^\circ$ ; the second, **iso-pentane**, **2-methylbutane** or **dimethylethylmethane**, boiling point  $27.9^\circ$ ; and the third, **2-2-dimethylpropane** or **tetramethylmethane**, boiling point,  $9.5^\circ$ .

n-Pentane is made thus:—

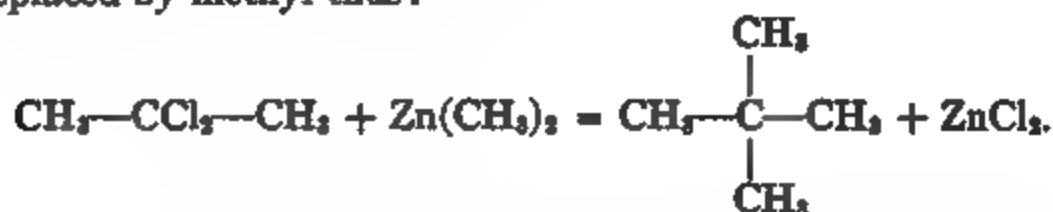


which shows its structure to be  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ . Dimethylethylmethane is made from isoamyl alcohol, which will be shown to have the formula,



by replacing the hydroxyl by hydrogen. Hence its structure is that represented above by formula (2) or (3).

Tetramethylmethane is made by starting with acetone. Acetone has been shown to consist of carbonyl in combination with two methyl groups, as represented in the formula  $\text{CH}_3\text{—CO—CH}_3$ . It has also been shown that, by treating acetone with phosphorus pentachloride, the oxygen is replaced by chlorine, giving a compound of the formula  $\text{CH}_3\text{—CCl}_2\text{—CH}_3$ . Now, by treating this chloride with zinc methyl, the chlorine is replaced by methyl thus:—



The product is tetramethylmethane, and this synthesis shows clearly what the structure of the hydrocarbon is. Normal and isopentane have been isolated from Pennsylvania petroleum. Tetramethylmethane is present in the gas from Caucasian and Rumanian petroleum.

The commercial pentane, boiling at  $25^\circ\text{--}40^\circ$ , used in the pentane lamp for determining the candle power of illuminating gas, consists largely of normal pentane and isopentane with small quantities of lower and higher homologues. It is also used in pentane thermometers for determining low temperatures.

**Hexanes.** — The student will now be prepared to apply the theory to the determination of the number of hexanes possible. He will find that there are five. The theory is, in this case, as in the preceding, in perfect accordance with the facts. There are five, and only five, hexanes known:—

1. **Normal hexane**,  $\text{CH}_3\text{.CH}_2\text{.CH}_2\text{.CH}_2\text{.CH}_2\text{.CH}_3$ , (b. p.  $68^\circ$ ) has been isolated from Pennsylvania petroleum. It is the principal constituent of volatile petroleum ether boiling at  $68^\circ\text{--}95^\circ$ .

2. **Dimethylpropylmethane**,  $\text{CH}_3\text{.CH}_2\text{.CH}_2\text{.CH} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ , is found in American and Rumanian petroleum (boiling point  $62^\circ$ ).

3. **Methyldiethylmethane**,  $\text{CH}_3 \cdot \text{CH} < \begin{smallmatrix} \text{CH}_3 \cdot \text{CH}_3 \\ \text{CH}_3 \cdot \text{CH}_3 \end{smallmatrix}$ , is present in Rumanian petroleum (b. p.  $64^\circ$ ).

4. **Dimethylisopropylmethane**,  $\begin{smallmatrix} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{smallmatrix} > \text{HC} - \text{CH} < \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ , occurs in Caucasian naphtha (b. p.  $58^\circ$ ).

5. **Trimethylethylmethane**,  $\text{H}_3\text{C} - \begin{smallmatrix} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{smallmatrix} - \text{CH}_2 \cdot \text{CH}_3$ , is found in

American and Caucasian naphtha (b. p.  $49.6^\circ$ ).

Passing upward, *nine* heptanes are possible according to the theory, while but *seven* have thus far been discovered; and, while theory indicates the possibility of the discovery of *eighteen* hydrocarbons of the formula  $\text{C}_8\text{H}_{18}$ , only *nine* are known. The theoretical number of isomeric varieties of the higher members of the series is very great, but our knowledge in regard to them is limited, and it is impossible to say whether the theory will ever be confirmed by facts. There are 802 possible isomers of the formula  $\text{C}_{13}\text{H}_{28}$ . It may be that there is some law limiting the number of complicated hydrocarbons. It is, however, idle to speculate upon the subject. It is well for us to keep in mind that a thorough knowledge of a few of the simplest members of the series is all that is necessary for the present.

*Normal heptane* occurs in the turpentine from *Pinus sabiniana*, a native of California.

On examining the formulas used to express the structure of the hydrocarbons, it will be found that they can be divided into three classes:—

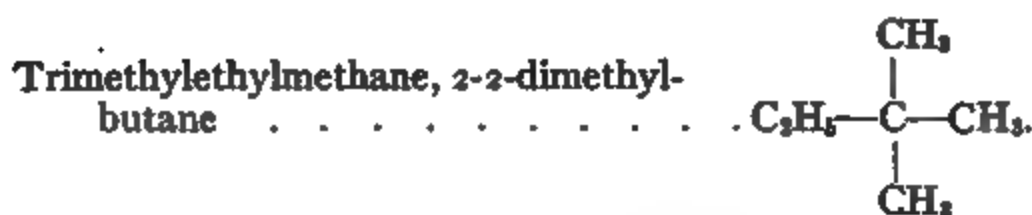
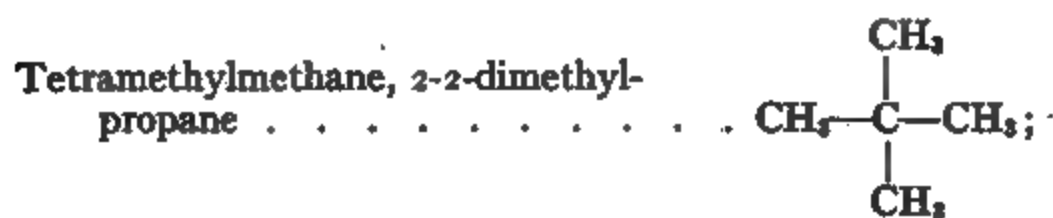
(1) Those in which there is no carbon atom in combination with more than two others; as:—

Propane . . . .	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3$ ;
Normal butane . .	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ ;
Normal pentane . .	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ ;
Normal hexane . .	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ .

(2) Those in which there is at least one carbon atom in combination with three others; as, —



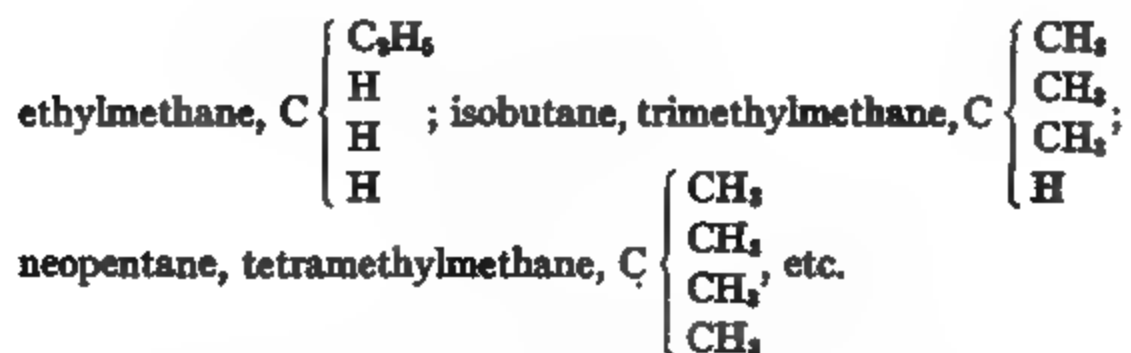
(3) Those in which there is at least one carbon atom in combination with four others; as: —



The members of the first class are called *normal paraffins*; those of the second class, *isoparaffins*; and those of the third class, *neoparaffins*.

Only the members of the same class are strictly comparable with one another. Thus it has been found that the boiling points of the normal hydrocarbons bear simple relations to one another, and that the same is true of the isoparaffins; but, on comparing the boiling points and other physical properties of normal paraffins with those of the iso or neoparaffins, no such simple relations are observed.


Regarding the names of the paraffins, the simplest nomenclature in use is that according to which the hydrocarbons are all regarded as derivatives of methane. Thus propane is



*Geneva nomenclature.* — The nomenclature for the hydrocarbons recommended by the International Congress of Chemists at Geneva retains the names used at present for the normal hydrocarbons. For example, pentane is the compound  $CH_3(CH_2)_3CH_3$ . In the case of the iso and the neohydrocarbons, the longest normal chain gives the name, the other groups present being regarded as substituents. The position of the groups is indicated by numbering the carbon atoms in the normal chain. Thus isobutane is 2-methylpropane, isopentane is 2-methylbutane, and tetramethylmethane is 2,2-dimethylpropane (127).

## CHAPTER IX

### OXYGEN DERIVATIVES OF THE HIGHER MEMBERS OF THE PARAFFIN SERIES

 THE derivatives of the higher members of the paraffin series will now be taken up. Not much need be said in regard to the halogen derivatives. A few of them will be mentioned in connection with the corresponding alcohols. The chief substances that will require attention are the alcohols and acids.

#### ALCOHOLS

**Normal propyl alcohol, propanol-1,  $C_3H_7OH$ .**—When sugar undergoes alcoholic fermentation with yeast, some propyl alcohol is always formed, and is contained in "fusel oil" (4 to 7 per cent). From this it can be separated by fractional distillation.

It is a colorless liquid with an alcoholic odor. It boils at  $97.19^\circ$ .

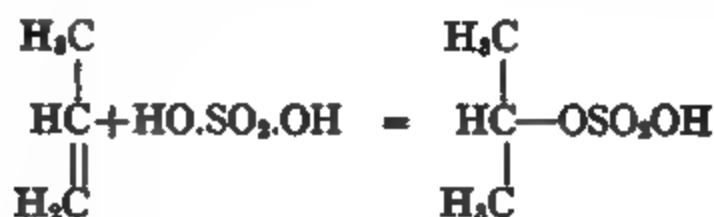
**NOTE FOR STUDENT.**—Compare with the boiling points of methyl and ethyl alcohol.

It conducts itself like the first two members of the series. By oxidation it is converted into propionic aldehyde,  $C_3H_6O$ , and propionic acid,  $C_3H_6O_2$ , which bear to it the same relations that acetic aldehyde and acetic acid bear to ethyl alcohol. It is therefore a primary alcohol (132).

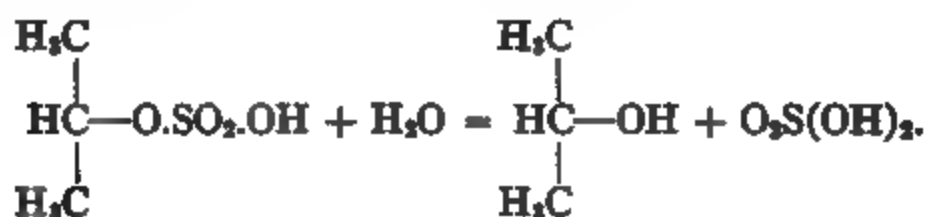
**Secondary propyl or isopropyl alcohol, propanol-2,  $C_3H_7OH$ .**—The reasons for regarding the alcohols as hydroxyl derivatives of the hydrocarbons have been given. As the six hydrogen atoms of ethane are all of the same kind, but one ethyl alcohol is possible, and only one is known. But just as there are two butanes or methyl derivatives of propane, so there are two hydroxyl derivatives of propane, or two propyl alcohols. The

first is the one obtained from "fusel oil," the other is the one called secondary propyl alcohol. This has already been referred to under Acetone (74), where it was stated that acetone is converted into secondary propyl alcohol by nascent hydrogen. In fact this is one of the methods for the preparation of the alcohol.

Isopropyl alcohol is now made on the large scale from propylene obtained in the "cracking" (118) of petroleum. The propylene is absorbed in sulphuric acid, giving isopropyl acid sulphate:—



When this is diluted with water and distilled it gives isopropyl alcohol:—



Like ethyl alcohol it forms a constant boiling mixture with water. This boils at  $80.37^\circ$  at  $760^{\text{mm}}$ . It contains 87.9 per cent isopropyl alcohol and 12.1 per cent water. It is used as a solvent and for the preparation of isopropyl compounds, *e.g.* isopropyl acetate. It is sold under the name *Petrohol*.

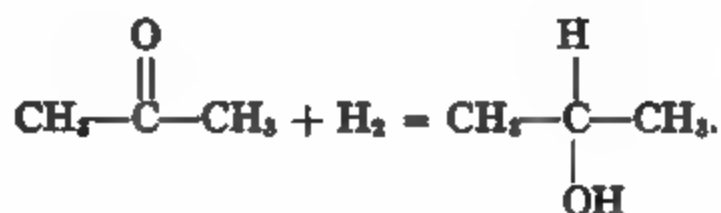
It is, like ordinary propyl alcohol, a colorless liquid. When pure it boils at  $82^\circ$ . While all its reactions show that it is a hydroxide, it conducts itself towards oxidizing agents quite differently from the alcohols thus far studied. It is converted first into acetone,  $\text{C}_3\text{H}_6\text{O}$ , which is isomeric with propionic aldehyde obtained from ordinary propyl alcohol; by further oxidation, this, however, does not yield an acid of the formula  $\text{C}_3\text{H}_6\text{O}_3$ , as we might expect, but breaks down, yielding two

simpler acids; viz., formic acid,  $\text{CH}_2\text{O}_2$ , and acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$  (74).

**Secondary alcohols.** — Secondary propyl alcohol is the simplest representative of a class of alcohols known as *secondary alcohols*. They are made by treating the ketones with nascent hydrogen, and are easily distinguished from the primary alcohols by their conduct towards oxidizing agents. They yield ketones containing the same number of carbon atoms, and then these break down, yielding acids containing a smaller number of carbon atoms.

Is there anything in the structure of these secondary alcohols to suggest an explanation of their conduct? Secondary propyl alcohol is made from acetone by treating this with nascent hydrogen. Acetone contains two methyl groups and carbonyl, as

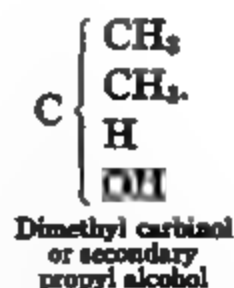
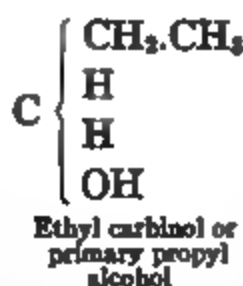
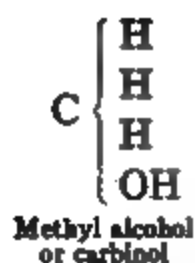
represented by the formula  $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ . The simplest change that can take place in this compound under the influence of hydrogen is that represented in the following equation: —



The very close connection existing between acetone and secondary propyl alcohol, and the fact that there are two methyl groups in acetone, make it appear probable that there are also two methyl groups in secondary propyl alcohol, as represented in the above formula.

On the other hand, the easy transformation of primary propyl alcohol into propionic acid,  $\text{H}_3\text{CCH}_2\text{COOH}$ , which will be shown to contain ethyl, shows that in the alcohol ethyl is also present. Therefore, we may conclude that the difference between primary and secondary propyl alcohol is that the former is an ethyl derivative and the latter a dimethyl derivative of methyl alcohol or carbinol as represented by the formulas: —





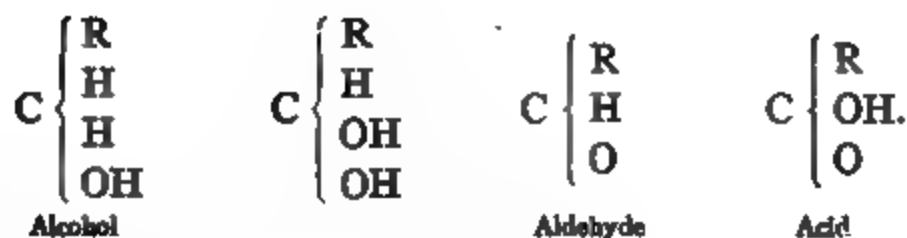
Primary propyl alcohol is *methyl alcohol or carbinol in which one hydrogen of the methyl group is replaced by a radical*, while secondary propyl alcohol is *methyl alcohol or carbinol in which two hydrogens are replaced by radicals*. An examination of all secondary alcohols known shows that the above statement can be made in regard to all of them. They must be regarded as derived from methyl alcohol by the substitution of *two* radicals for *two* hydrogen atoms and are therefore called *secondary alcohols*. The alcohols of the first class, like ethyl and ordinary propyl alcohol, are derived from methyl alcohol by the substitution of *one* radical for *one* hydrogen, and are hence called *primary alcohols*.

Another way of stating the difference between primary and secondary alcohols is this: Primary alcohols contain the univalent group  $\text{CH}_2\text{OH}$ ; secondary alcohols contain the bivalent group  $\text{CHOH}$ . These statements necessarily follow from the first ones.

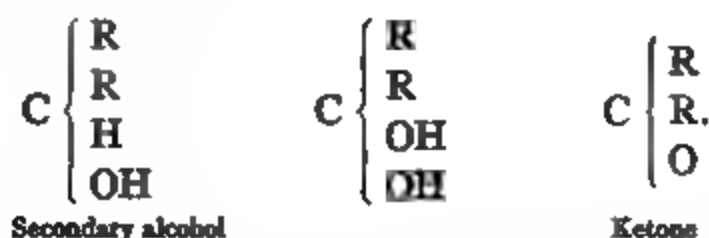
A primary alcohol, when oxidized, yields an aldehyde and then an acid containing the same number of carbon atoms as the alcohol.

A secondary alcohol, when oxidized, yields a ketone containing the same number of carbon atoms and then this yields acids containing a smaller number of carbon atoms.

Recalling what was said regarding the nature of the changes involved in passing from a primary alcohol to the corresponding aldehyde and acid, it will be seen that the formation of an acid containing the same number of carbon atoms is impossible in the case of a secondary alcohol. In the case of a primary alcohol, we have: —



In the case of the secondary alcohol, we have:—



Further introduction of oxygen cannot take place without a breaking down of the compound. It will be seen that the formulas used to express the structure of the compounds are in close accordance with the facts.

**Butyl alcohols,  $\text{C}_4\text{H}_9\text{OH}$ .**—Theoretically, there are two possible hydroxyl derivatives of each of the two butanes, making four butyl alcohols in all. They are all known. Two are primary alcohols.

1. **Normal butyl alcohol, butanol-1,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,** boiling point  $117.7^\circ$ , gives *n*-butyric acid on oxidation.

Normal butyl alcohol is now made on the large scale by the fermentation of Indian corn, employing an anaërobic organism (Weizmann process). The distillate from the fermented mash contains butanol (56 per cent), acetone (32 per cent), and ethyl alcohol (12 per cent). These are separated by subsequent rectification. The butyl alcohol is sold under the trade name *Butanol*. It is used chiefly in the lacquer industry and as a solvent for all kinds of resins and, after conversion into butyl acetate, in the manufacture of leather substitutes.

2. **Isobutyl alcohol, 2-methylpropanol-1,**  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 > \text{CH} \end{array} \text{CH}_2\text{OH}$ ,

b. p.  $108^\circ$ , gives isobutyric acid on oxidation.

Isobutyl alcohol is obtained on the large scale by fractional distillation of fusel oil, which contains from 15 to 25 per cent of this alcohol.

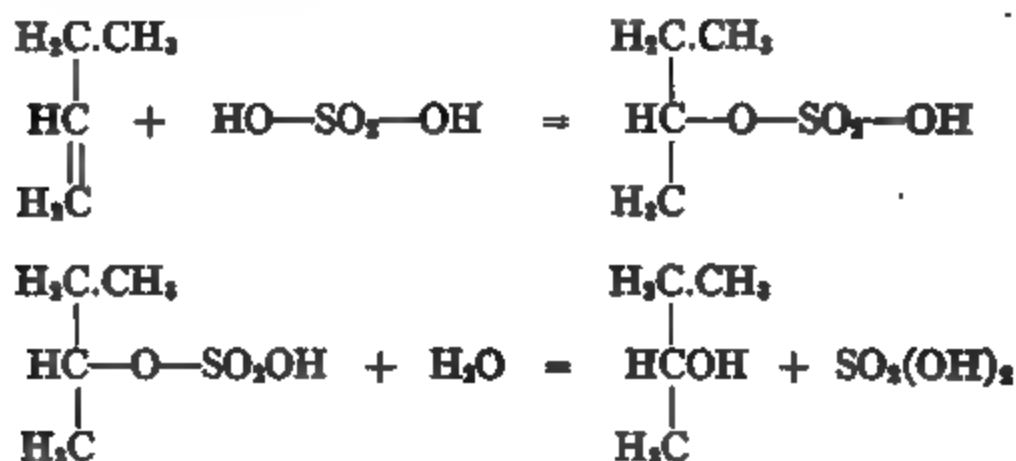
3. **Secondary butyl alcohol, butanol-2**,  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$  (b. p.  $99.9^\circ$ ), is made by treating ethylmethyl ketone with nascent hydrogen:—



and gives methylethyl ketone on oxidation.

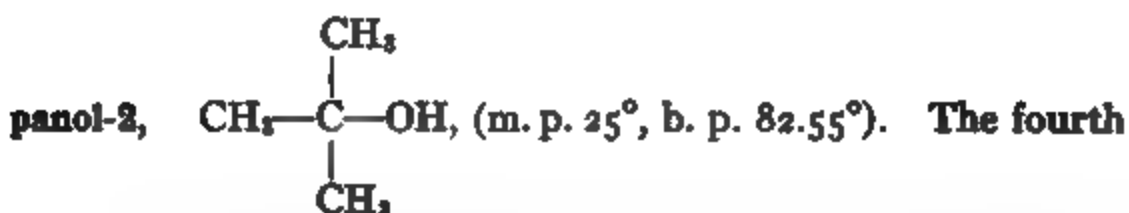
**NOTE FOR STUDENT.**—Compare this with the reaction for making secondary propyl alcohol.

This alcohol is also made from butylene in the same way that isopropyl alcohol is made from propylene (130).



Butylene, like propylene, is contained in the mixture of gases formed in the "cracking" of petroleum.

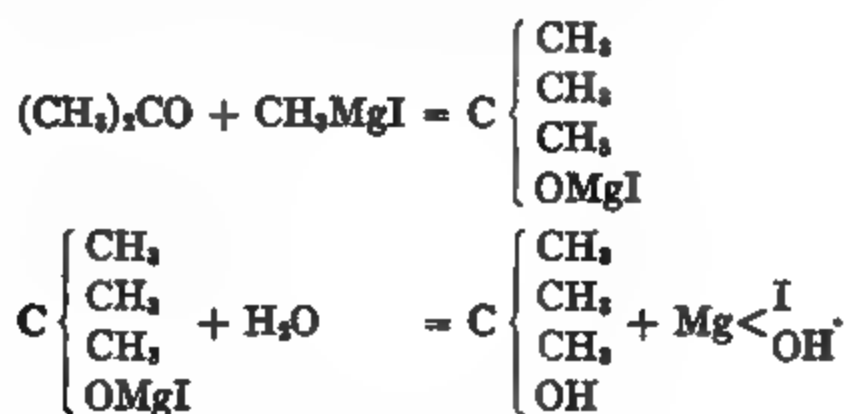
4. **Tertiary butyl alcohol, trimethyl carbinol, 2-methylpro-**



butyl alcohol has properties that distinguish it from the primary and secondary alcohols. When oxidized it yields neither an aldehyde nor a ketone containing the same number of carbon atoms, but breaks down at once, yielding compounds containing a smaller number of carbon atoms. Assuming that every primary alcohol contains the group  $\text{CH}_2\text{OH}$ , and that every secondary alcohol contains the group  $\text{CHOH}$ , it follows that

the two primary butyl alcohols and secondary butyl alcohol must have the formulas above assigned to them; and it follows further that the fourth butyl alcohol must have the above formula, as this represents the only other arrangement of the groups possible, according to the theory. This formula represents a condition that does not exist in either the primary or secondary alcohols. It is methyl alcohol in which all *three* hydrogen atoms of the methyl group are replaced by methyl groups. Such an alcohol is hence known as a *tertiary alcohol*, and the one under consideration is called *tertiary butyl alcohol*. It is the simplest representative of the class of tertiary alcohols. It contains the trivalent group C(OH).

Tertiary butyl alcohol is made by treating acetone with methyl magnesium iodide,  $\text{CH}_3\text{MgI}$  (Grignard reagent), and then treating this product with water:—



By using other ketones and magnesium compounds, other tertiary alcohols can be obtained.

With hydriodic acid tertiary butyl alcohol gives tertiary butyl iodide, and this gives isobutane when reduced with nascent hydrogen. Isobutyl alcohol, when treated in a similar manner, also gives isobutane. The other two butyl alcohols give normal butane.

**NOTE FOR STUDENT.**—Write the equations.

*Characteristics of the three classes of alcohols.* To recapitulate, the hydroxyl derivatives of the hydrocarbons can be divided into three classes, according to their conduct towards oxidizing agents.

To what was said regarding the conduct of primary and secondary alcohols on oxidation we may now add: Tertiary alcohols do not yield aldehydes, acids, or ketones containing the same number of carbon atoms, but break down, yielding compounds containing a smaller number of carbon atoms.

The formulas representing the three classes of alcohols are:—



**Pentyl alcohols, amyl alcohols,  $\text{C}_5\text{H}_{11}\text{OH}$ .** — Eight of these are possible, and all are known. Only two of the *amyl alcohols* need be taken up here.

**Inactive isoamyl alcohol, isobutyl carbinol, 3-methylbutanol-1,  $\text{CH}_3 > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$ .** — This alcohol, together with at least one other of the same composition, forms the chief part of "fusel oil." By fractional distillation of this, a mixture of two amyl alcohols called *fermentation amyl alcohol* is obtained, as a colorless liquid, having a penetrating odor, and boiling at  $128^\circ$  to  $132^\circ$ . This can be separated into two isomeric alcohols, one of which is *inactive* isoamyl alcohol (87 per cent), (b. p.  $131^\circ$ ), and the other *active* amyl alcohol (13 per cent), (b. p.  $128^\circ$ ). The names refer to the behavior of the substances towards polarized light, the former having no action upon it, the latter turning the plane of polarization to the left.

The method of separating the two alcohols is as follows: Fermentation amyl alcohol (b. p.  $128^\circ$ – $132^\circ$ ) is converted into the two amyl acid sulphates by means of concentrated sulphuric acid, and the barium salts of these are separated by fractional crystallization. The barium salt of the active amyl acid sulphate is more than twice as soluble as that of the inactive salt. The *pure* barium salts are then decomposed separately by dilute sulphuric acid and the alcohols recovered by boiling with water and distilling. In this way the pure inactive isoamyl

alcohol and the pure levorotatory amyl alcohol have been obtained.

When treated with oxidizing agents inactive isoamyl alcohol yields an acid containing the same number of carbon atoms, and is, therefore, a primary alcohol. The acid has been made by simple reactions which show that it must be represented by

the formula  $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . (See Valeric Acid, 147.)

Therefore, the alcohol has the structure represented by the above formula.

Active amyl alcohol, secondary butyl carbinol, 2-methylbutanol-1,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2\text{OH} \\ \text{CH}_3 \end{smallmatrix}$ .— This, as stated above, is obtained, together with the inactive isoamyl alcohol, from fusel oil. It is a primary alcohol as it gives *active* valeric acid on oxidation (147).

There are two active amyl alcohols known, one of which is dextrorotatory and the other levorotatory. Both turn the plane of polarized light the same number of degrees, one to the right and the other to the left. A mixture of the two, in equimolecular proportions, is, therefore, optically inactive. All three of these alcohols have been proved to have the *same structure* represented by the above formula, as they all give valeric acids,  $\text{H}_3\text{C} - \text{CH}_2 - \text{CH} < \begin{smallmatrix} \text{CH}_3 \\ \text{COOH} \end{smallmatrix}$ , on oxidation. We have here to deal with a new kind of isomerism. Compounds may conduct themselves chemically in the same way and yet differ in some of their physical properties, as in their action toward polarized light.

An ingenious hypothesis has been put forward to explain that particular kind of isomerism which shows itself in the action of organic compounds in the liquid or gaseous state or in solution, upon polarized light. Our ordinary structural formulas have nothing whatever to do with the relations of the atoms and groups in *space*. They indicate chemical *relations* that are discovered by a study of *chemical reactions*.

Let us suppose that in a carbon compound the carbon atom

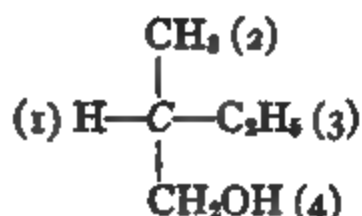
is situated at the centre of a tetrahedron, and that the four atoms or groups which it holds in combination are at the angles of the tetrahedron, as represented in figures below. If these groups are all *different in kind*, and *only in this case*, it is possible to arrange them in two ways in space with reference to the central carbon atom. The two arrangements are shown in the figures.



The difference between the two arrangements in space is that which is observed between either one and its reflection in a mirror, or between a right hand and a left hand.<sup>1</sup>

A carbon atom in combination with four different kinds of atoms or groups is called an *asymmetric* carbon atom. Whenever, therefore, a compound contains an asymmetric carbon atom, there are two possible arrangements of its parts in space, which correspond to the right-handed and the left-handed tetrahedron. It can be shown that if the arrangement of the groups in one of these figures rotates the plane of polarized light to the right (clockwise), the other will rotate it the *same* number of degrees to the left (counter-clockwise).

In active amyl alcohol there is an asymmetric carbon atom as shown in the formula

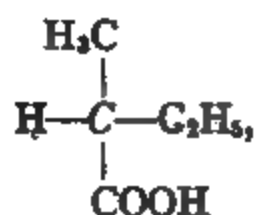


the central carbon atom appearing in combination with (1) hydrogen, (2) methyl, (3) ethyl, and (4) the primary alcohol

<sup>1</sup> This can be made clearer by means of models which can easily be constructed of stout wire and corks.

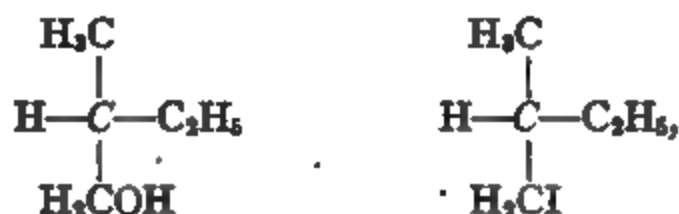
group. Hence, according to the hypothesis just stated, there are two possible arrangements in space of the constituents of this compound, one corresponding to the right-handed tetrahedron and the other to the left-handed tetrahedron. Both are secondary butyl carbinols, *i.e.* they are structurally identical. The inactive variety is formed by a combination of the two active compounds.

On oxidation *active* amyl alcohol gives *active* valeric acid,



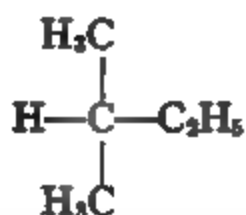
as the asymmetric carbon atom is still present in this compound.

If the *active* amyl alcohol is treated with hydriodic acid, it gives *active* amyl iodide,



as this compound also contains an asymmetric carbon atom.

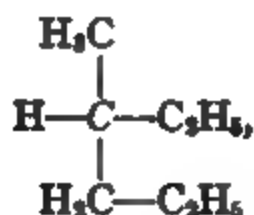
When this is treated with nascent hydrogen it gives isopentane,



and *isopentane is optically inactive*. It does not contain an asymmetric carbon atom, as two of the groups are now the same. Both *d*-amyl alcohol and *l*-amyl alcohol give isopentane, and hence it will be seen that this kind of isomerism is due to the asymmetric carbon atom, for it *disappears when the asymmetric carbon atom disappears*.

If, however, the *active* amyl iodide is treated with ethyl iodide and sodium, a heptane results,





and this is *optically active*, as it still contains an asymmetric carbon atom.

The branch of chemistry that has to deal with this kind of isomerism is called *stereochemistry*. The phenomena of stereochemistry have been the subject of extensive investigations and the facts established furnish a strong foundation for the theory expounded above.<sup>1</sup>

Commercial *isoamyl acetate*,  $\text{C}_8\text{H}_{18}\text{O} \cdot \text{CO} \cdot \text{CH}_3$ , (boiling point  $138.5^\circ$ – $139^\circ$ ), is made from fermentation amyl alcohol (b. p.  $128^\circ$ – $132^\circ$ ), acetic acid, and a small quantity of sulphuric acid. It is burned in the Hefner lamp to determine the candle power of illuminating gas. Its chief use, however, is as a solvent in the preparation of lacquers (*Zapon*) and of leather substitutes (*Fabrikoid*) and in the manufacture of fruit essences.

*Isoamyl nitrite*,  $\text{C}_5\text{H}_{11}\text{O} \cdot \text{NO}$ , a yellow fluid with a fruity odor, (boiling point  $97^\circ$ – $98^\circ$ ), is made from fermentation amyl alcohol by the action of nitrous acid. It is used in the preparation of diazonium and isonitroso compounds, and in medicine, particularly in cases of angina pectoris.

A list of some of the more important members of the series is given below. In naming the alcohols, it is best to refer them to methyl alcohol, just as the hydrocarbons are referred to marsh gas. Calling methyl alcohol *carbinol*, we get such names as methylcarbinol, diethylcarbinol, etc., which convey at once an accurate idea concerning their structure. A few illustrations will suffice. Take the alcohols above:—



<sup>1</sup> See *Stereochemistry*, by A. W. Stewart, second edition (1919).

Primary propyl alcohol is <i>ethylcarbinol</i> ,	C	$\begin{cases} \text{CH}_3\text{CH}_2 \\ \text{H} \\ \text{H} \\ \text{OH} \end{cases}$ ;
Secondary propyl alcohol is <i>dimethylcarbinol</i> ,	C	$\begin{cases} \text{CH}_3 \\ \text{CH}_3 \\ \text{H} \\ \text{OH} \end{cases}$ ;
Tertiary butyl alcohol is <i>trimethylcarbinol</i> ,	C	$\begin{cases} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{OH} \end{cases}$ ;
Inactive isoamyl alcohol is <i>isobutylcarbinol</i> ,	C	$\begin{cases} \text{CH}_2\text{CH} < \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \\ \text{H} \\ \text{H} \\ \text{OH, etc., etc.,} \end{cases}$

*Geneva nomenclature.*—The “official” names of the alcohols end in “-ol,” the normal primary alcohols being designated as methanol, ethanol, propanol, butanol, pentanol, etc., while isobutyl alcohol is called 2-methylpropanol-1; isoamylalcohol, 3-methylbutanol-1; and active amyl alcohol, 2-methylbutanol-1. In the case of the secondary alcohols the position of the hydroxyl group is given, thus, propanol-2 is secondary propyl alcohol and butanol-2 is secondary butyl alcohol. In the case of the tertiary alcohols the positions of the hydrocarbon residue and the hydroxyl group are both designated, thus, trimethyl carbinol is 2-methylpropanol-2.

*Cetyl alcohol*,  $\text{C}_{18}\text{H}_{37}\text{OH}$ , in the form of the palmitic ester, is the chief constituent of spermaceti.

*Ceryl alcohol*,  $\text{C}_{26}\text{H}_{53}\text{OH}$ , as the cerotic ester is found in Chinese wax.

*Myricyl alcohol*,  $\text{C}_{20}\text{H}_{41}\text{OH}$ , occurs in beeswax and in carnauba wax as the palmitic ester.

The alcohols are obtained from these esters by saponification with alcoholic caustic potash. Of most of the higher members only the normal primary alcohol is known.

The following table will give some idea of the extent to which the series of alcohols derived from the paraffins has been investigated. There are *fourteen* hexyl alcohols and *fourteen* heptyl alcohols known.

#### ALCOHOLS OF THE METHYL ALCOHOL SERIES

##### SERIES $C_nH_{2n+1}.OH$

Methyl alcohol, b. p. 64.7°	. . . . .	$CH_3.OH$
Ethyl " 78.32	. . . . .	$C_2H_5.OH$
n-Propyl " 97.19	. . . . .	$C_3H_7.OH$
n-Butyl " 117.7	. . . . .	$C_4H_9.OH$
n-Pentyl " 137.8	. . . . .	$C_5H_{11}.OH$
n-Hexyl " 156.8	. . . . .	$C_6H_{13}.OH$
n-Heptyl " 175.8	. . . . .	$C_7H_{15}.OH$
n-Octyl " 195.5	. . . . .	$C_8H_{17}.OH$
n-Nonyl " 213.5	. . . . .	$C_9H_{19}.OH$
Cetyl " m. p. 48	. . . . .	$C_{16}H_{33}.OH$
Ceryl " m. p. 79	. . . . .	$C_{26}H_{53}.OH$
Myricyl " m. p. 88	. . . . .	$C_{26}H_{53}.OH$

#### 2. ALDEHYDES

It follows from what has been said concerning the properties of primary alcohols, that there should be an aldehyde corresponding to every primary alcohol. Many of these have been prepared. They resemble ordinary acetic aldehyde so closely that it is unnecessary to take them up individually. If the structure of the alcohol from which an aldehyde is formed by oxidation is known, the structure of the aldehyde is also known.

Besides the one method for the preparation of aldehydes that has been mentioned, viz., the oxidation of primary alcohols, there is one other that should be specially noted. It consists in distilling calcium formate with the calcium salt of a higher fatty acid. Thus, when a mixture of calcium acetate and calcium formate is distilled, acetic aldehyde is formed as represented by the equation:—



This method has been used to a considerable extent in making the higher members of the series.

### 3. ACIDS

Formic and acetic acids are the first two members of an homologous series of similar acids, called the *fatty acids* because several of them occur in large quantities as glycerol esters in the natural fats. The names and formulas of some of the principal members are given in the following table. The reasons for representing the acids as compounds containing the carboxyl group,  $\text{CO}_2\text{H}$ , have already been given.

FATTY ACIDS			
SERIES $\text{C}_n\text{H}_{2n+1}\cdot\text{CO}_2\text{H}$ , or $\text{C}_n\text{H}_{2n}\text{O}_2$			
Formic acid	b. p. 100.8°	. . . . .	$\text{H}\cdot\text{CO}_2\text{H}$
Acetic "	118.7	. . . . .	$\text{CH}_3\cdot\text{CO}_2\text{H}$
Propionic "	141	. . . . .	$\text{C}_2\text{H}_5\cdot\text{CO}_2\text{H}$
n-Butyric "	162.4	. . . . .	$\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$
n-Valeric "	185.4	. . . . .	$\text{C}_4\text{H}_9\cdot\text{CO}_2\text{H}$
n-Caproic or Hexoic acids }	205	. . . . .	$\text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$
Enanthylic or n-Heptoic acids }	223	. . . . .	$\text{C}_6\text{H}_{13}\cdot\text{CO}_2\text{H}$
Caprylic or Octoic acids }	m. p. 16.5	. . . . .	$\text{C}_7\text{H}_{15}\cdot\text{CO}_2\text{H}$
Pelargonic or Nonic acids }	12.5	. . . . .	$\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$
Capric acid	31.4	. . . . .	$\text{C}_9\text{H}_{19}\cdot\text{CO}_2\text{H}$
Lauric "	44	. . . . .	$\text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\text{H}$
Myristic acid	54	. . . . .	$\text{C}_{13}\text{H}_{27}\cdot\text{CO}_2\text{H}$
Palmitic "	62.6	. . . . .	$\text{C}_{15}\text{H}_{31}\cdot\text{CO}_2\text{H}$
Margaric "	60	. . . . .	$\text{C}_{16}\text{H}_{33}\cdot\text{CO}_2\text{H}$
Stearic "	69.3	. . . . .	$\text{C}_{17}\text{H}_{35}\cdot\text{CO}_2\text{H}$
Arachidic "	77	. . . . .	$\text{C}_{19}\text{H}_{39}\cdot\text{CO}_2\text{H}$
Behenic "	84	. . . . .	$\text{C}_{21}\text{H}_{43}\cdot\text{CO}_2\text{H}$
Hyenic "	77-78	. . . . .	$\text{C}_{24}\text{H}_{49}\cdot\text{CO}_2\text{H}$
Cerotic "	78.5	. . . . .	$\text{C}_{26}\text{H}_{53}\cdot\text{CO}_2\text{H}$
Melissic "	91	. . . . .	$\text{C}_{29}\text{H}_{59}\cdot\text{CO}_2\text{H}$

**Propionic acid, propane acid,  $C_3H_5O_2(C_2H_4.CO_2H)$ .** — Propionic acid is formed in small quantity (1) by the distillation of wood; (2) by the fermentation of calcium lactate or malate with certain microorganisms; (3) by heating ethyl cyanide (propionitrile) with a solution of caustic potash: —



and (4) by oxidizing normal propyl alcohol with chromic acid. This last method is used on the large scale.

Other methods for preparing it are the following: —

(1) By reducing lactic acid or acrylic acid with hydriodic acid. (This will be explained under Lactic acid and Acrylic acid.)

(2) By the action of carbon dioxide upon sodium ethyl: —



It is a colorless liquid with a penetrating odor somewhat resembling that of acetic acid. It boils at  $141^\circ$ .

NOTE FOR STUDENT. — Compare with boiling points of formic and acetic acids.

It yields a large number of derivatives corresponding to those obtained from acetic acid.

NOTE FOR STUDENT. — What is propionyl chloride? and how can it be prepared? It is analogous to acetyl chloride.

The monosubstitution products of propionic acid present an interesting and instructive case of isomerism. There are two chloropropionic acids, two bromopropionic acids, etc. Those products which are obtained by direct treatment of propionic acid with substituting agents are called  $\alpha$ -products, and the isomeric substances  $\beta$ -products. Thus we have  *$\alpha$ -chloropropionic* (b. p.  $186^\circ$ ), and  *$\alpha$ -bromopropionic acid* (b. p.  $204^\circ$ ), made by treating propionic acid with chlorine or bromine;  *$\beta$ -chloropropionic acid* (m. p.  $41.5^\circ$ , b. p.  $204^\circ$ ), and  *$\beta$ -bromopropionic acid* (m. p.  $62.5^\circ$ ), made by treating acrylic acid (286) with hydrochloric or hydrobromic acid. The usual method of representation indicates the possibility of the existence of two isomeric

chloropropionic acids, and of similar monosubstitution products of propionic acid. The acid is represented thus:—



Now, if chlorine should enter into the compound, as represented by the formula  $\text{CH}_3\text{Cl}.\text{CH}_2.\text{CO}_2\text{H}$ , (1) we should have one of the chloropropionic acids; while, if it should enter as indicated in the formula  $\text{CH}_3.\text{CHCl}.\text{CO}_2\text{H}$ , (2) we should have the isomeric product. There are two chloropropionic acids actually known, and the theory gives two formulas. How can we tell which of the formulas represents  $\alpha$ -chloropropionic acid, and which the  $\beta$ -acid? Only by carefully studying the reactions and methods of formation of both compounds. The best evidence is furnished by a study of the lactic acids, which will be shown to be monohydroxypropionic acids.  $\alpha$ -chloropropionic acid can be transformed into one of the lactic acids,  $\alpha$ -hydroxypropionic acid, by heating with water:—



The structure of this acid is represented by the formula  $\text{CH}_3.\text{CH}(\text{OH})\text{CO}_2\text{H}$ , and by replacing the hydroxyl of this lactic acid by chlorine,  $\alpha$ -chloropropionic acid is formed. It therefore follows that formula (2) above given is that of  $\alpha$ -chloropropionic acid, and formula (1) that of  $\beta$ -chloropropionic acid. Further, any monosubstitution product of propionic acid that can be made directly from  $\alpha$ -chloropropionic acid, or converted directly into this acid, is an  $\alpha$ -product, and has the general formula:—



and, similarly, the  $\beta$ -products have the general formula:—



in which X represents any univalent atom or group.

It will be noted that the  $\alpha$ -substitution products contain an asymmetric carbon atom, while the  $\beta$ -products do not. Optically active  $\alpha$ -chloro- and  $\alpha$ -bromopropionic acids have been isolated.

**Butyric acid,  $C_4H_8O_2$  ( $C_3H_7.CO_2H$ ).** — **Normal butyric acid, butane acid,  $CH_3.CH_2.CH_2.CO_2H$ .** When butter which contains 2–3 percent of *n*-butyric acid is boiled with a solution of caustic potash the potassium salts of butyric acid and of some of the higher members of the series are found in the solution at the end of the operation. Butter, like other fats, belongs to the class of compounds known as ethereal salts; and these, as we have seen, when boiled with solutions of the alkalies, are saponified, yielding an alcohol and alkali salts of the acids (saponification). In the case of butter and of nearly all other fats, the alcohol formed is *glycerol*. Butyric acid occurs in other fats besides butter, and free in perspiration and in the feces. It also occurs in many plants in the form of esters.

It is most readily made by the butyric acid fermentation of sugar in the presence of chalk.

Other methods for the preparation of butyric acid are: —

- (1) By oxidation of normal butyl alcohol; and
- (2) By heating normal propyl cyanide,  $CH_3.CH_2.CH_2CN$ , with a solution of caustic potash.

The acid is a liquid having an acid, rancid odor, like that of rancid butter. It boils at  $162.4^\circ$ . Like the lower members of the series it mixes with water in all proportions at ordinary temperatures.

*Ethyl butyrate*,  $C_3H_7.CO_2C_2H_5$  (b. p.  $120^\circ$ ), has a pleasant odor resembling that of pineapples. It is used under the name of *essence of pineapples*. Its alcoholic solution forms the artificial banana oil.

**Isobutyric acid, methylpropane acid,  $\begin{smallmatrix} CH_3 \\ | \\ CH_3 \end{smallmatrix} > CH.CO_2H$ .** —

From the two propyl alcohols the two chlorides, propyl chloride,  $CH_3.CH_2.CH_2Cl$ , and isopropyl chloride,  $\begin{smallmatrix} CH_3 \\ | \\ CH_3 \end{smallmatrix} > CHCl$ , can be made, and from these the corresponding cyanides, —

Propyl cyanide . . . . .  $CH_3.CH_2.CH_2CN$ , ;

and Isopropyl cyanide . . . . .  $\begin{smallmatrix} CH_3 \\ | \\ CH_3 \end{smallmatrix} > CHCN$ .

When boiled with a solution of caustic potash, the former is

converted into normal butyric acid, as stated above; while the latter yields isobutyric acid,  $\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CO}_2\text{H}$ . This acid can also be prepared by oxidizing isobutyl alcohol,



It is found in nature in the carob bean (St. John's bread).

Isobutyric acid is a liquid that boils at  $155.5^\circ$ . Its odor is less unpleasant than that of the normal acid.

**Valeric acids,  $\text{C}_5\text{H}_{10}\text{O}_2$  ( $\text{C}_4\text{H}_9 \cdot \text{CO}_2\text{H}$ ).** — Four carboxyl derivatives of the butanes are possible. Four acids of the formula  $\text{C}_5\text{H}_{10}\text{O}_2$  are known.

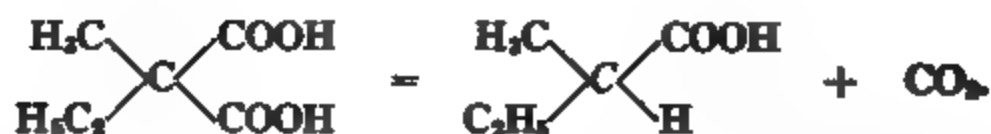
**Isovaleric acid,  $\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .** — This acid is made by oxidizing isoamyl alcohol. It can also be made (and this reaction reveals the structure of the acid) by starting with isobutyl alcohol  $\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2\text{OH}$ , converting this first into the chloride and then into the cyanide, and, finally, transforming the cyanide,  $\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2\text{CN}$ , into the acid. It occurs in valerian root, whence its name. It is a liquid of unpleasant odor, boiling at  $174^\circ$ .

*Isoamyl isovalerate,  $\text{C}_4\text{H}_9 \cdot \text{CO}_2\text{C}_5\text{H}_{11}$* , has the odor of apples, and is used under the name of *essence of apples*.

**Active valeric acids,  $\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{HO}_2\text{C} \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_3$ .** — These acids are prepared by oxidation of the active amyl alcohols. Although the alcohol turns the plane of polarization to the left, the acid turns it to the right. The alcohol is *levorotatory*, and the acid *dextrorotatory*. The levo acid has also been isolated. The *dl*-acid (optically inactive) has been made synthetically. All have the same boiling point,  $177^\circ$ . These acids contain an asymmetric carbon atom. (See Active amyl alcohol, 137.)

The *dl*-acid is obtained by heating methylethylmalonic acid (161) to its melting point: —





Compounds containing an asymmetric carbon atom, when prepared synthetically, are almost always equimolecular mixtures of the two optically active forms and are hence optically inactive by external compensation.

The higher acids of the series are found in various fats. They are difficultly soluble in water. The highest members are solids insoluble in water. The two best-known, because occurring in largest quantity, are *palmitic* and *stearic acids*. These occur in the form of esters of glycerol, in all the common fats which will be treated of under Glycerol (164).

**Palmitic acid**,  $\text{H}_5\text{C}(\text{CH}_2)_{14}\text{CO}_2\text{H}$  occurs, together with stearic, oleic, and other fatty acids, as esters of glycerol in vegetable and animal fats. For example, it is found in butter, human fat, olive oil, cocoanut oil, bayberry tallow, and in large quantity in palm oil, whence its name. It also occurs in the form of esters of the monacid alcohols as waxes, *e.g.* spermaceti (cetyl palmitate). It is best made from palm oil or bayberry tallow by boiling with caustic soda and decomposing the sodium palmitate formed by means of dilute sulphuric acid: the precipitated palmitic acid is then repeatedly crystallized from hot alcohol until it has the correct melting point,  $62.6^\circ$ .

**Stearic acid**,  $\text{H}_5\text{C}(\text{CH}_2)_{16}\text{CO}_2\text{H}$  (m. p.  $69.3^\circ$ ), in the form of esters of glycerol, is found in many fats, especially tallows, as mutton suet and beef suet. It is best prepared from the commercial stearic acid of which "stearin" candles are made. This consists essentially of a mixture of stearic and palmitic acids. By dissolving this mixture in hot alcohol and adding a hot alcoholic solution of magnesium acetate, a precipitate of almost pure magnesium stearate is obtained. This is washed with alcohol, dried, decomposed with hydrochloric acid, and the stearic acid recrystallized from alcohol until it has the correct melting point.

Compared with the strong mineral acids, like hydrochloric acid, the fatty acids are all very weak acids.

**Soaps.**<sup>1</sup> — In speaking of the decomposition of ethereal salts by boiling with solutions of the alkalies, it was stated that this process is called saponification because it is best exemplified in the manufacture of soaps from fats. The fats are themselves rather complicated ethereal salts. When they are boiled with a solution of an alkali, as caustic soda, glycerol is liberated, and the alkali salts of the acids are formed. *These salts are called soaps.*

Soaps soluble in water are the potassium or sodium salts of palmitic, stearic, and oleic acids, the hard soaps being the sodium salts, principally of the solid fatty acids, while the soft soaps are potassium salts, chiefly oleates. The soaps are "salted out" of their aqueous solutions by the addition of common salt, as they are insoluble in the brine formed. The potassium soaps are converted into the sodium soaps by this "salting out" process. These soaps form a clear solution when dissolved in a little water, but in a larger quantity of water they are partially hydrolyzed, yielding free alkali and the free fatty acid or an acid salt. The cleansing action of soap is usually attributed to the presence of the small amount of free alkali formed:—



This hydrolysis is analogous to that which takes place with inorganic salts of a weak acid with a strong base, and increases on dilution. It is, however, probable that the cleansing action of soap is largely due to its power to emulsify oils and fats.

The calcium, barium, and magnesium soaps are insoluble in water, and hence a precipitate of the calcium soap is formed when "hard" water is used with soap. The lead soaps are formed by boiling fats with lead oxide and water, and were formerly used in medicine under the name of "lead plaster." Lead and manganese soaps (made from linseed oil), dissolved in linseed oil and thinned with turpentine or benzine, form the liquid "driers" of the painters, used to hasten the drying of raw linseed oil.

<sup>1</sup> See article on Soap in Thorpe's *Dictionary of Applied Chemistry*.

Floating soaps are sodium soaps, usually made from cocoanut oil, in which the specific gravity of the soap is lowered by filling the soap with minute air bubbles.

The so-called "liquid soaps," so much used in lavatories, are solutions of potassium cocoanut-oil soaps and glycerol in water. They usually contain from 15 to 20 per cent anhydrous soap and from 5 to 10 per cent glycerol. Some contain glucose in the place of glycerol. Many of them contain a small amount of free oleic acid.

Calcium soaps, usually called lime soaps, made by the action of slaked lime on fats, are used in large quantities in the manufacture of lubricating greases.

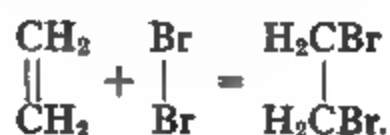
Zinc stearate is used in toilet powders.

## POLYACID ALCOHOLS AND POLYBASIC ACIDS

### 1. DIACID ALCOHOLS

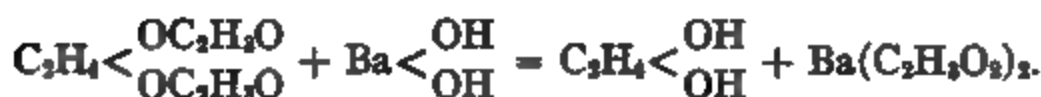
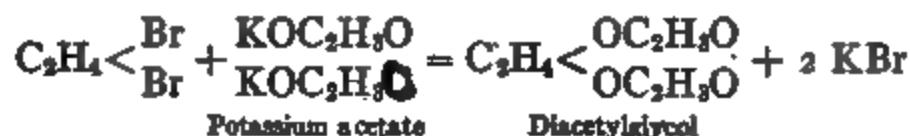
The alcohols thus far treated of are the simplest kind. They correspond to the simplest metallic hydroxides, as potassium hydroxide, KOH. Just as these simplest metallic hydroxides are called *monacid bases*, so the simplest alcohols are called *monacid alcohols*. But, as is well known, there are metallic hydroxides, like calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , barium hydroxide,  $\text{Ba}(\text{OH})_2$ , etc., that contain two hydroxyls, and are hence known as *diacid bases*; and so, too, there are *diacid alcohols* that bear to the monacid alcohols the same relation that the diacid bases bear to the monacid bases. Only one alcohol of this kind, derived from the paraffin hydrocarbons, is important enough to call for treatment here.

Ethylene alcohol or glycol, ethanediol,  $\text{C}_2\text{H}_6\text{O}_2$ ,  $\text{C}_2\text{H}_4(\text{OH})_2$ .—Glycol is made by starting with ethylene, a hydrocarbon of the formula  $\text{C}_2\text{H}_4$ . When this is brought together with bromine, the two unite directly, forming *ethylene bromide*,  $\text{C}_2\text{H}_4\text{Br}_2$ :—

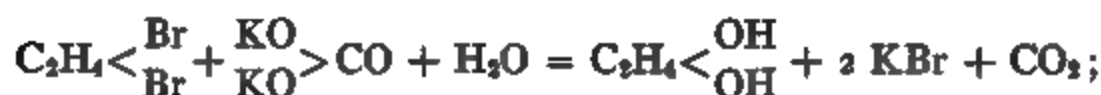


By replacing the two bromine atoms by hydroxyls, ethylene alcohol or glycol is formed.

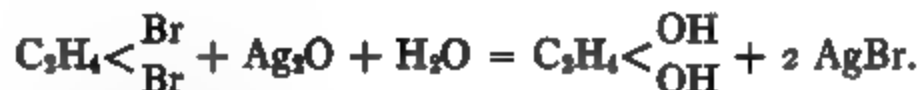
The reactions involved are represented by the following equations:—



Glycol can also be made by heating ethylene bromide with a solution of potassium carbonate:—

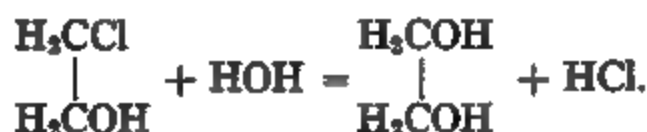


and by heating ethylene bromide with silver oxide and water:—

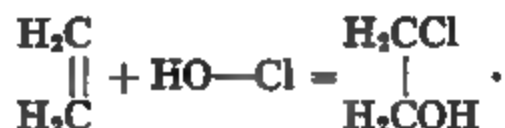


These methods of formation show clearly that ethylene alcohol is the dihydroxyl derivative of ethane.

Ethylene alcohol is now made on the large scale by hydrolyzing ethylene chlorohydrin with water:—



The ethylene chlorohydrin is made by passing ethylene into aqueous hypochlorous acid:—



Glycol is a colorless, inodorous, somewhat sirupy liquid, that boils at  $197^\circ$ . It has a sweetish taste, and was hence called *glycol* (Gr. *glykys*, *sweet*). The other diacid alcohols

of this series are also called *glycols*. It is miscible in all proportions with water and alcohol, but is not very soluble in ether. It is not poisonous.

The derivatives of ethylene alcohol are not so numerous as those of the better known members of the methyl alcohol series, but those which are known are of the same general character. The reactions of the alcohol are the same as those of the monacid alcohols, but it presents more possibilities. In most cases in which a monacid alcohol yields one derivative, ethylene alcohol yields two. Thus, with sodium, the two compounds, *sodium glycol*,  $C_2H_4<\begin{smallmatrix} ONa \\ OH \end{smallmatrix}$ , and *disodium glycol*,  $C_2H_4<\begin{smallmatrix} ONa \\ ONa \end{smallmatrix}$ , have been obtained; from these, by treating with ethyl iodide, the two ethers, *ethyl glycol ether*,  $C_2H_4<\begin{smallmatrix} OC_2H_5 \\ OH \end{smallmatrix}$ , and *diethyl glycol ether*,  $C_2H_4<\begin{smallmatrix} OC_2H_5 \\ OC_2H_5 \end{smallmatrix}$ , are made. By treatment with hydrochloric acid, the chloride,  $C_2H_4<\begin{smallmatrix} OH \\ Cl \end{smallmatrix}$ , known as *ethylene chlorohydrin*, is formed from glycol; and by treatment with phosphorus pentachloride, ethylene chloride,  $C_2H_4Cl_2$ , results.

*Ethylene chlorohydrin*,  $\begin{smallmatrix} H_2CCl \\ | \\ H_2COH \end{smallmatrix}$  is a liquid boiling at  $132^\circ$  and miscible with water. It is the monochlorine substitution product of ethyl alcohol and yields ethyl alcohol on reduction and monochloroacetic acid on oxidation. When distilled with a solution of caustic potash it gives *ethylene oxide*: —



This is a liquid of ethereal odor boiling at  $12.5^\circ$ , miscible with water and gradually combining with it to form glycol. It is

isomeric with acetic aldehyde, which is ethylidene oxide  $\begin{smallmatrix} H_2C \\ | \\ HCO \end{smallmatrix}$ .

Ethylene chlorohydrin and ethylene oxide are characterized by great chemical reactivity, and they are hence used in the

preparation of a large number of organic substances. Ethylene chlorohydrin combines with aniline to give hydroxyethyl-aniline, and this is used in the manufacture of indigo on the large scale in Germany.

With sodium sulphide, ethylene chlorohydrin gives thiodiglycol,  $S < \begin{smallmatrix} CH_2CH_2OH \\ CH_2CH_2OH \end{smallmatrix}$ , which is converted into mustard gas (79) by the action of strong hydrochloric acid. This is the method by which mustard gas was first made during the World War.

The conduct of glycol towards acids is like that of a diacid base. It forms *neutral* and *alcoholic esters*, of which the acetates may serve as examples. Thus we have the

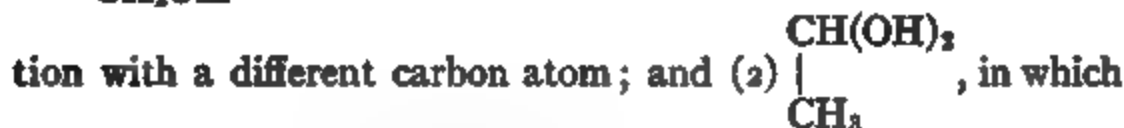


the former still containing alcoholic hydroxyl and corresponding to a basic salt; the latter being a neutral compound.

When acetyl chloride acts upon the alcohol at ordinary temperature, the product has the formula  $C_2H_4 < \begin{smallmatrix} OC_2H_3O \\ Cl \end{smallmatrix}; -$



There are two ways in which the structure of a compound of the formula  $C_2H_4(OH)_2$  can be represented. These are, —



both hydroxyls are represented in combination with the same carbon atom. The question suggests itself, to which of these formulas does ethylene alcohol correspond? To answer this question,

recall what was said regarding the two dichloroethanes (32), known as *ethylene chloride* and *ethylidene chloride*. The former of these corresponds to the formula  $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ , while the latter, which is formed from aldehyde by replacing the carbonyl oxygen by two chlorine atoms (50), is represented by the formula  $\text{CHCl}_2.\text{CH}_3$ . When the chlorine atoms of ethylene chloride are replaced by hydroxyls, ethylene alcohol is produced. Hence, the alcohol has the formula  $\text{HOH}_2\text{C}-\text{CH}_2\text{OH}$ , or each of the hydroxyls is in combination with a different carbon atom. When oxidized, ethylene alcohol gives, first, glycolic

acid,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COOH} \end{array}$ , and then oxalic acid,  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ . This furnishes

independent evidence that the alcohol contains two primary alcohol groups, and it must therefore be represented by the

formula  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ .

All attempts to make the isomeric diacid alcohol corresponding to ethylidene chloride, and having both hydroxyls in combination with the same carbon atom, as represented in the

formula  $\begin{array}{c} \text{CH}(\text{OH})_2 \\ | \\ \text{CH}_3 \end{array}$ , have failed. Instead of getting ethylidene

alcohol, aldehyde is obtained. Aldehyde is ethylidene alcohol minus water:—



It is believed that one carbon atom cannot, under ordinary conditions, hold in combination more than one hydroxyl group. If this is true, then ethylidene alcohol cannot be prepared any more than the hypothetical carbonic acid,  $\text{OC} < \begin{array}{c} \text{OH} \\ \text{OH} \end{array}$ , can be. So, too, the simplest diacid alcohol conceivable, *viz.*, methylene alcohol,  $\text{CH}_2(\text{OH})_2$ , cannot exist, but would break down, if formed at all, into water and formic aldehyde:—



(See, however, Chloral hydrate (54) and discussion regarding the oxidation of alcohol to aldehyde (65).)

Ethyl alcohol, as was pointed out, may be regarded either as ethane in which one hydrogen is replaced by hydroxyl, or as water in which one hydrogen is replaced by ethyl. Ethyl, like all the radicals contained in the monacid alcohols, is *univalent*. It is ethane less one atom of hydrogen, just as methyl is methane less one atom of hydrogen. Each has the power of uniting with one atom of hydrogen, or another univalent element, or of taking the place of one atom of hydrogen.

If two atoms of hydrogen are taken from methane and ethane, the residues or radicals  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  are left. These can unite with two atoms of hydrogen, or take the place of two atoms of hydrogen, and they are hence called *bivalent radicals*.

Just as ethylene alcohol is regarded as ethane in which two hydrogen atoms are replaced by two hydroxyls, so it may be regarded as water in which the bivalent radical ethylene replaces two hydrogens belonging to two different molecules of water:—

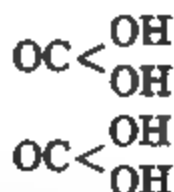


## 2. DIBASIC ACIDS $\text{R}''(\text{CO}_2\text{H})_2$

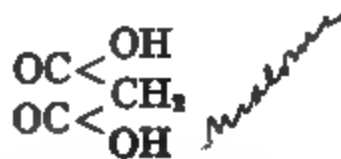
Just as there are diacid alcohols derived from the paraffins, so there are dibasic acids which are regarded as derivatives of the paraffins. It has been shown that the simplest acids, the monobasic fatty acids, are closely related to formic and carbonic acids; that they are to be regarded as derived from the latter by replacement of a hydroxyl by a radical, or as derived from the paraffins by the introduction of the carboxyl group,  $\text{CO}_2\text{H}$ . The conditions existing in this group are essential to the acid properties. If two carboxyls are introduced into marsh gas, a substance of the formula  $\text{CH}_2(\text{CO}_2\text{H})_2$  is formed, and this is a dibasic acid. It contains two acid hydrogens, and is capable of forming two series of salts, the acid and neutral salts, like other dibasic acids. It may be regarded also as



derived from two molecules of carbonic acid by the replacement of two hydroxyls by the bivalent radical  $\text{CH}_2$ :—



Two molecules carbonic acid



Dibasic acid

The general methods of preparation available for the building up of the series of dibasic acids are modifications of those used in making the monobasic acids. They are:—

1. *Oxidation of diacid primary alcohols.* Just as a monobasic acid primary alcohol,  $\text{R} \cdot \text{CH}_2\text{OH}$ , yields by oxidation a monobasic acid, so a diacid primary alcohol,  $\text{R}''(\text{CH}_2\text{OH})_2$ , yields a dibasic acid,  $\text{R}''(\text{CO}_2\text{H})_2$ .

2. *Hydrolysis of the dicyanides,  $\text{R}''(\text{CN})_2$ , with solutions of the caustic alkalis.*

3. *Oxidation of the primary alcohol acids.* These are compounds which are at the same time alcohol and acid; as, for example, hydroxyacetic acid, which is acetic acid in which one of the hydrogen atoms of the hydrocarbon residue, methyl, has been replaced by hydroxyl, as represented in the formula



When this is oxidized the alcoholic group,  $\text{CH}_2\text{OH}$ , is converted into carboxyl, and oxalic acid, a dibasic acid, is formed.

4. *From the cyanogen derivatives of the monobasic acids, such as cyanacetic acid,  $\text{CH}_2 < \begin{array}{c} \text{CN} \\ \text{CO}_2\text{H} \end{array}$ , by the hydrolysis of the cyanogen group into carboxyl.*

#### DIBASIC ACIDS, $\text{C}_n\text{H}_{2n-2}\text{O}_4$

		M. P.	K = IONIZATION CONSTANT	
Oxalic acid	. . . . .	189.5° <sup>1</sup>	10.0	$(\text{CO}_2\text{H})_2$
Malonic "	. . . . .	135.6	0.163	$\text{CH}_2(\text{CO}_2\text{H})_2$
Succinic "	. . . . .	182.8	0.0065	$(\text{CH}_2)_2(\text{CO}_2\text{H})_2$

<sup>1</sup> Anhydrous acid.

DIBASIC ACIDS (*Continued*)

	M. P.	K = IONIZATION CONSTANT	
Glutaric acid . . . . .	97.5	0.0047	$(\text{CH}_2)_3(\text{CO}_2\text{H})_2$
Adipic " . . . . .	183	0.0037	$(\text{CH}_2)_4(\text{CO}_2\text{H})_2$
Pimelic " . . . . .	105	0.0032	$(\text{CH}_2)_5(\text{CO}_2\text{H})_2$
Suberic " . . . . .	140	0.0026	$(\text{CH}_2)_6(\text{CO}_2\text{H})_2$
Azelaic " . . . . .	106.5		$(\text{CH}_2)_7(\text{CO}_2\text{H})_2$
Sebacic " . . . . .	134.5		$(\text{CH}_2)_8(\text{CO}_2\text{H})_2$
Brassylic " . . . . .	112		$(\text{CH}_2)_{11}(\text{CO}_2\text{H})_2$
Roccellic " . . . . .	132		$(\text{CH}_2)_{15}(\text{CO}_2\text{H})_2$

The members of this series differ from one another by  $\text{CH}_2$  or a multiple of this, but while in the paraffin series this difference is due to the substitution of methyl for hydrogen, this may or may not be the case in this series. This will appear as the individual members are taken up, though it is obvious that the second member, malonic acid, is not a methyl derivative of oxalic acid. In the case of the higher members of the series there are two possibilities.

**Oxalic acid, ethane diacid,  $\text{C}_2\text{H}_2\text{O}_4$ ,  $(\text{CO}_2\text{H})_2$ .** — In one sense, according to the accepted definition, oxalic acid is not a member of the series with which we are dealing, as it is not derived from a hydrocarbon by replacement of two hydrogen atoms by two carboxyl groups; nor is it derived from two molecules of carbonic acid by replacement of two hydroxyls by a bivalent radical. Still it is in other respects so closely allied to the members of the series, and has so many reactions in common with the other members, that it must necessarily be taken up here.

Oxalic acid occurs very widely distributed in nature; as in certain plants of the *oxalis* varieties, in the form of the acid potassium salt; as the calcium salt in many plants and in urinary calculi; and as the ammonium salt in guano.

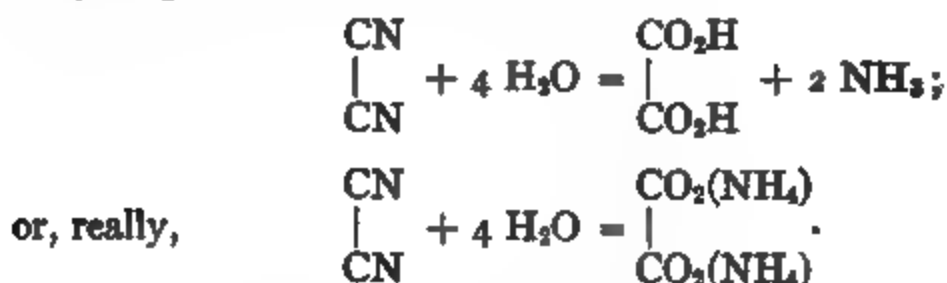
It is formed by the action of nitric acid upon many organic substances, particularly the different varieties of sugar and the carbohydrates, such as starch, cellulose, etc.

On the large scale, oxalic acid is made by heating wood shavings or sawdust with caustic potash and caustic soda to  $240^\circ$

to 250°. The mass is extracted with water, and the solution evaporated to the specific gravity 1.35, when sodium oxalate crystallizes out on cooling. The crystallized sodium oxalate is dissolved in boiling water, boiled with milk of lime, the precipitate of calcium oxalate extracted several times with boiling water, and decomposed with dilute sulphuric acid. After filtering, the solution of oxalic acid is then evaporated to specific gravity 1.116, and allowed to stand until the gypsum has settled, filtered, and evaporated to crystallization. It is purified by recrystallizing several times from water.

Other methods are the following:—

1. The spontaneous transformation of an aqueous solution of cyanogen:—



2. Heating carbon dioxide with sodium:—



3. Heating sodium formate to 360°:—



This method is now used on the large scale for the manufacture of sodium oxalate and from it oxalic acid.

Oxalic acid is a very much stronger acid than its homologues, as is shown by its ionization constant. (See table (156).)

Oxalic acid crystallizes from water in monoclinic prisms containing two molecules of water ( $\text{C}_2\text{H}_2\text{O}_4 + 2 \text{H}_2\text{O}$ ) which melt at 101.5°. It loses this water at 100°, and then melts at 189.5°. It sublimes at 157°, but, if heated higher, it breaks down into carbon monoxide, carbon dioxide, formic acid, and water:—



Sulphuric acid decomposes it into carbon monoxide, carbon

dioxide, and water. Heated with glycerol to  $110^{\circ}$ , carbon dioxide and formic acid are formed (see Formic acid, 54): —



It is an excellent reducing agent, and is used to standardize solutions of potassium permanganate.

It is used in bleaching leather, in laundries to remove ink and rust spots, in bleaching straw goods, in cleaning powders, as a solvent for Prussian blue in making blue ink, in the preparation of dyes, as a reagent in analytical chemistry, and in photography. It is also used in dyeing and in calico printing.

Oxalic acid is poisonous.

*Salts of oxalic acid.* Like all dibasic acids, oxalic acid forms acid and neutral salts with metals. All the salts are insoluble except those of the alkali metals and the ammonium salts. Among those most common are the *acid potassium salt*,  $\text{C}_2\text{O}_4\text{HK}$ , which is found in the sorrels or plants of the *oxalis* variety; the *ammonium salt*,  $\text{C}_2\text{O}_4(\text{NH}_4)_2$ ; and *calcium oxalate*,  $\text{C}_2\text{O}_4\text{Ca}$ , which, being insoluble in water and acetic acid, is used as a means of detecting calcium in the presence of magnesium, and of estimating calcium and oxalic acid.

**Malonic acid, propane diacid,  $\text{CH}_2(\text{CO}_2\text{H})_2$ .** — This acid was first made by oxidation of malic acid (193), and was hence called *malonic acid*. It can best be made by starting with acetic acid. The necessary steps are: (1) making chloroacetic acid; (2) transforming chloroacetic acid into cyanacetic acid; (3) heating cyanacetic acid with a solution of an alkali.

NOTE FOR STUDENT. — Write the equations representing the three steps mentioned.

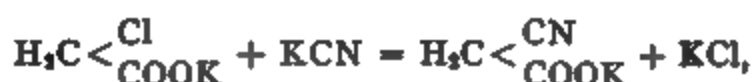
It is a solid that crystallizes in laminæ. It breaks down at a temperature above  $135.6^{\circ}$ , which is its melting point, into carbon dioxide and acetic acid: —



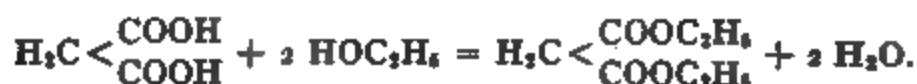
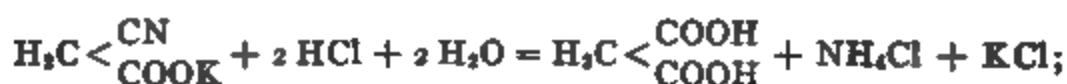
*All organic acids with two carboxyl groups attached to the same carbon atom lose a molecule of carbon dioxide when heated above their melting points.*

Diethyl malonate,  $\text{H}_2\text{C} < \begin{smallmatrix} \text{COOC}_2\text{H}_5 \\ \text{COOC}_2\text{H}_5 \end{smallmatrix}$ , is made from monochloroacetic

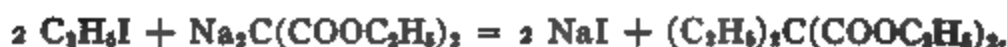
acid by first heating with potassium cyanide: —



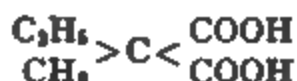
and then converting the cyanacetic acid thus formed into the ester by the action of alcoholic hydrochloric acid: —



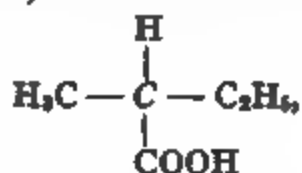
It boils at  $198^\circ$ . The two methylene hydrogen atoms are replaceable by sodium, giving a monosodium,  $\text{H} > \text{C}(\text{COOC}_2\text{H}_5)_2$ , and a disodium salt,  $\text{Na}_2\text{C}(\text{COOC}_2\text{H}_5)_2$ . When these are heated with ethyl iodide, esters of the homologues of malonic acid are obtained: —



When these esters are hydrolyzed the homologues of malonic acid result:  $(\text{C}_2\text{H}_5)\text{CH}(\text{COOH})_2$  and  $(\text{C}_2\text{H}_5)_2\text{C}(\text{COOH})_2$ . These, when heated to their melting points, lose carbon dioxide, just as malonic acid does, and give homologues of acetic acid. By means of this "malonic ester synthesis," as it is called, a large number of the homologues of malonic and acetic acids have been made. It is possible to introduce two different alkyl groups into the ester. Thus if the monoethyl derivative obtained above is treated with sodium, it gives  $\begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{Na} \end{smallmatrix} > \text{C}(\text{COOC}_2\text{H}_5)_2$ , which with methyl iodide gives  $\begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{smallmatrix} > \text{C}(\text{COOC}_2\text{H}_5)_2$ , and this when hydrolyzed gives methylethyl-malonic acid,

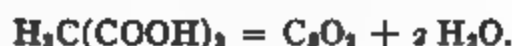


When heated above its melting point this loses carbon dioxide and gives methylethylacetic acid,



or *dl*-valeric acid, which can be resolved into its optically active components. (See Valeric acid 147 and Lactic acid 152.)

Carbon Suboxide,  $\text{C}_3\text{O}_2$ , is formed in small quantity when dry malonic acid is distilled in a vacuum with phosphorus pentoxide:—



It is a gas with a pungent odor. It condenses to a liquid boiling at  $7^\circ$ . With water it forms malonic acid. At ordinary temperatures it polymerizes to a reddish black, amorphous mass. It may have the constitution represented by the formula,  $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$ .

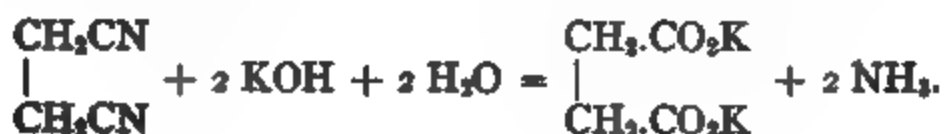
Succinic acids,  $\text{C}_4\text{H}_6\text{O}_4$ ,  $\text{C}_2\text{H}_4(\text{CO}_2\text{H})_2$ . — Regarding these acids as derived from ethane by the substitution of two carboxyls for two hydrogens, it is clear that two are possible, one corresponding to ethylene chloride and another to ethylidene chloride. Two are actually known. One is the well-known *succinic acid*; the other is called *isosuccinic acid*.

Succinic acid, ethylenesuccinic acid, butane diacid,  
 $\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\ | \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$  . — This acid occurs in amber (hence its name, from

Lat. *succinum*, amber); in some varieties of lignite; in many plants; and in the animal organism.

It is formed under many conditions, especially by oxidation of fats with nitric acid, by fermentation of calcium malate with certain microorganisms, and, in small quantity, in the alcoholic fermentation of sugar. Among the methods for its preparation are:—

1. Hydrolysis of ethylene cyanide (made from ethylene bromide) with a solution of a caustic alkali:—



2. Similarly, by the hydrolysis of  $\beta$ -cyanpropionic acid (made from  $\beta$ -iodopropionic acid (190)) with a solution of an alkali.

NOTE FOR STUDENT. — What is  $\beta$ -cyanpropionic acid?

3. Reduction of tartaric and malic acids by means of hydriodic acid. These well-known acids will be shown to be hydroxyl derivatives of succinic acid, and the reaction here mentioned will be explained. The methods actually used in the preparation of succinic acid are: (1) the distillation of amber, and (2) the fermentation of ammonium tartrate with certain bacteria.

The acid crystallizes in monoclinic prisms, that melt at  $182.8^\circ$ . It boils at  $235^\circ$ , at the same time giving off water, and yielding the *anhydride*: —



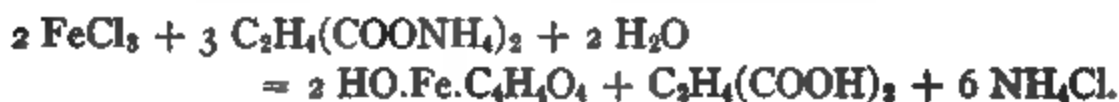
Succinic anhydride is a solid substance that crystallizes well from a mixture of chloroform and toluene. It melts at  $120^\circ$ , and boils at  $261^\circ$ . It is best made by the action of thionyl chloride on the acid: —



It is converted into succinic acid by boiling with water. When boiled with alcohols it yields the corresponding ester acids. For example, with ordinary alcohol monoethyl succinate is formed: —



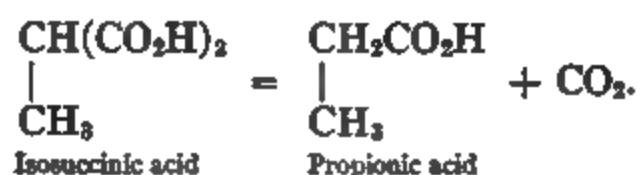
Among the salts *basic ferric succinate*,  $\text{C}_4\text{H}_4\text{O}_4 \cdot \text{Fe}(\text{OH})$ , is of special interest, as it is entirely insoluble in water, and can therefore be used for the purpose of separating iron and aluminium from manganese, zinc, nickel, and cobalt quantitatively: —



**Isosuccinic acid, ethylidenesuccinic acid,**  $\begin{array}{c} \text{CH}(\text{CO}_2\text{H})_2 \\ | \\ \text{CH}_3 \end{array}$ . This acid is made by hydrolyzing  $\alpha$ -cyanpropionic acid (made from  $\alpha$ -bromopropionic acid) with a solution of an alkali.

NOTE FOR STUDENT. — What is  $\alpha$ -cyanpropionic acid and how is it made?

Isosuccinic acid forms crystals that melt with decomposition between  $120^\circ$ – $135^\circ$ . Heated above its melting point it breaks down into propionic acid and carbon dioxide: —

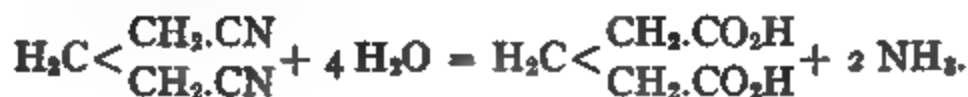


Isosuccinic acid is a methyl derivative of malonic acid. Ordinary succinic acid is not.

NOTE FOR STUDENT. — Note carefully the difference between the two succinic acids, as shown by their conduct when heated. What is the difference?

**Acids of the formula  $\text{C}_5\text{H}_8\text{O}_4$ ,  $\text{C}_5\text{H}_8(\text{CO}_2\text{H})_2$ .** — Four acids of the formula  $\text{C}_5\text{H}_8\text{O}_4$  are known, only one of which, however, need be mentioned here.

**Glutaric acid, pentane diacid,  $\text{CH}_2(\text{CH}_2\text{COOH})_2$ ,** made by the hydrolysis of trimethylene cyanide: —



It melts at  $97.5^\circ$  and is soluble in water, alcohol, and in ether.

## TRIACID ALCOHOLS

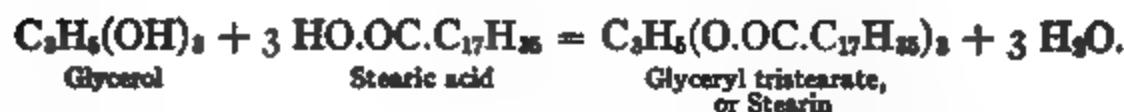
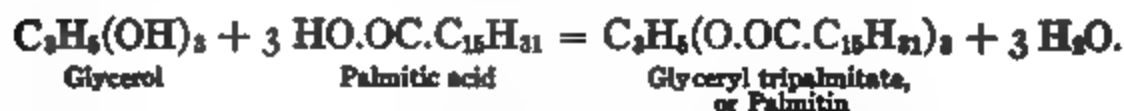
The existence of monacid alcohols corresponding to the monacid bases, like potassium hydroxide, and of diacid alcohols corresponding to the diacid bases, like calcium hydroxide, suggests the possible existence of *triacid alcohols* corresponding to triacid bases, like ferric hydroxide. There is only one alcohol



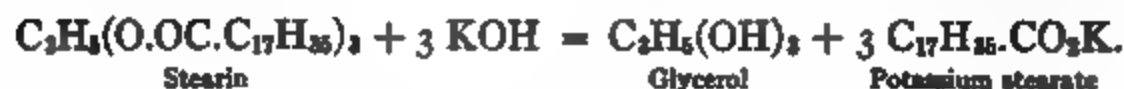
of this kind derived from the paraffin hydrocarbons that is at all well known. This is the common substance glycerin or glycerol.

Glycerol, glycerin, propane triol 1,2,3,  $C_3H_8O_3$ . — As has been stated repeatedly, glycerol (commonly called glycerin) occurs very widely distributed as the alcoholic constituent of the fats. The acids with which it is in combination are mostly members of the fatty acid series, though one, *oleic acid*, which is found frequently, is a member of the acrylic acid series (286). Besides oleic acid the two acids most frequently met with in fats are palmitic and stearic acids. When a fat is saponified with caustic potash, it yields free glycerol and the potassium salts of the acids. The reactions involved in the synthesis of palmitin and stearin and in the saponification of these fats are: —

#### Formation



#### Saponification



#### MANUFACTURE OF GLYCEROL AND FATTY ACIDS

Besides this method of saponifying the fats by alkalies used in soap-making, glycerol is made on the large scale as a by-product of the manufacture of candles. Several methods are used to hydrolyze the fats into free fatty acids and glycerol, of which the following are the most important: —

(1) By heating with water under pressure in an autoclave, a small quantity of lime, magnesia, or zinc oxide being added to aid the hydrolysis.

(2) By heating with concentrated sulphuric acid to 120°.

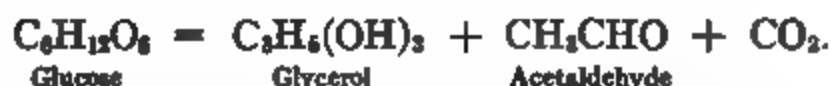
This method not only hydrolyzes the fats into glycerol and fatty acids, but also converts the liquid oleic acid into a solid fatty acid. (See Oleic acid.)

(3) By heating with water and Twitchell's reagent. This reagent is made by heating commercial oleic acid and an aromatic hydrocarbon, like naphthalene, with concentrated sulphuric acid and washing out the excess of sulphuric acid with water.

(4) By means of a fat-splitting enzyme, lipase, found in castor oil seed (*Ricinus communis*).

The aqueous solution of glycerol obtained in these processes is concentrated to remove water, and the glycerol is purified by distillation in a vacuum. The purest glycerol on the market is that used in making nitroglycerin. This is usually distilled a second time, in order to remove as much water as possible and to eliminate impurities that might cause explosions when the glycerol is used in the manufacture of nitroglycerin.

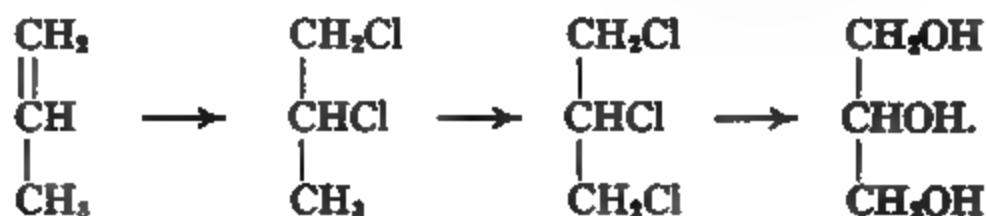
*Formation and synthesis.* — Glycerol is formed in small quantity (about 3 per cent of the sugar used) in the fermentation of sugar with yeast. This amount may be increased to 38 per cent by bringing about the fermentation of the sugar solution in the presence of large amounts of sodium sulphite. Under these conditions the amount of alcohol formed is diminished while the amount of glycerol is increased. An equivalent quantity of acetic aldehyde (which combines with the sodium bisulphite produced by the action of carbon dioxide on the sodium sulphite) is produced together with glycerol:—



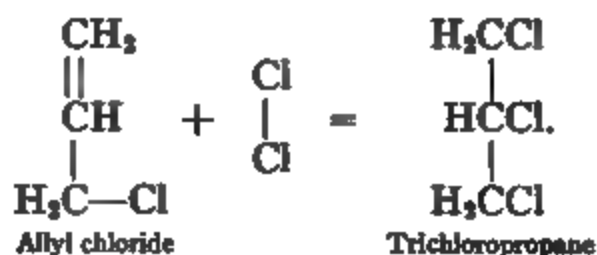
It will be seen from this that glycerol and acetic aldehyde are intermediate products in the fermentation of sugar by yeast to alcohol and carbon dioxide. During the World War over a million kilograms of glycerol per month were made in Germany from beet sugar molasses by this method.

Glycerol has been made synthetically from propylene chloride,  $\text{C}_3\text{H}_7\text{Cl}_2$ , made from propylene (279) and chlorine. The neces-

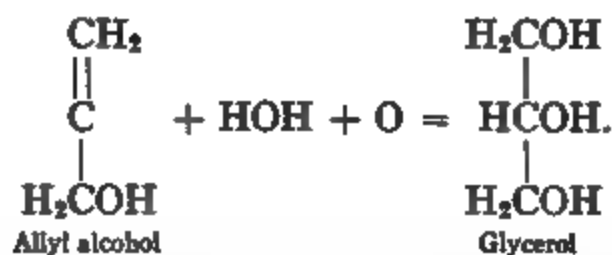
sary steps are: (1) treatment with iodine chloride, giving  $C_3H_5Cl_3$ ; (2) treatment of the trichloropropane with water, thus replacing the three chlorine atoms by hydroxyl groups:—



That each chlorine atom in trichloropropane is connected with a different carbon atom follows from its synthesis from allyl chloride and chlorine:—



(3) Another method that leads to the synthesis of glycerol consists in oxidizing allyl alcohol (283). This reaction is represented thus:—



*Properties.*—Glycerol is a syrupy colorless liquid, with a sweetish taste. (Compare with glycol.) It mixes with alcohol and water in all proportions, but is insoluble in ether. At low temperatures it slowly solidifies, forming deliquescent crystals which melt at  $20^\circ$ . Pure glycerol boils at  $290^\circ$  almost without decomposition. If salts are present, it undergoes decomposition at the boiling temperature. It is purified by distillation under diminished pressure. It is volatile with water vapor. It does not evaporate at ordinary temperatures. It attracts moisture from the air, and retains its oily feel. It makes the skin soft without objectionable results.

Glycerol finds extensive use in medicine, in the preparation of cosmetics, in the textile industry, in the manufacture of tobacco (to prevent drying), as a sweetening agent in the preparation of drinks, in the preparation of self-inking pads (to prevent the drying up of the ink), in the preparation of the ink rolls used in printing, in automobile radiators, gas meters, etc., to prevent freezing in cold weather. Its chief use is in the manufacture of *nitroglycerin*.

The world's production of glycerol is about 85,000 tons annually, most of which is made and used in this country. When glycerol is heated with a dehydrating agent, such as sodium bisulphate, it gives acrolein (285), and this fact is made use of as a test for glycerol or the fats. Another test for glycerol is to heat a borax bead moistened with the fluid in the flame of a bunsen burner. If glycerol is present, boric acid is set free and colors the flame green. The acid properties of glycerol are also shown by the fact that alkalis give no precipitate of copper hydroxide when added to a solution of copper sulphate containing glycerol. This is due to the formation of a soluble copper salt of glycerol. (See Fehling's solution.)

The reactions of glycerol all clearly lead to the conclusion that it is a triacid alcohol.

(1) The three hydroxyl groups can be replaced successively by chlorine, giving the compounds,—

*Monochlorohydrin*,  $\text{ClCH}_2\text{CHOHCH}_2\text{OH}$ ;

*Dichlorohydrin*,  $\text{ClCH}_2\text{CHOHCH}_2\text{Cl}$ ;

*Trichlorohydrin*,  $\text{ClCH}_2\text{CHClCH}_2\text{Cl}$ .

The last compound is really trichloropropane.

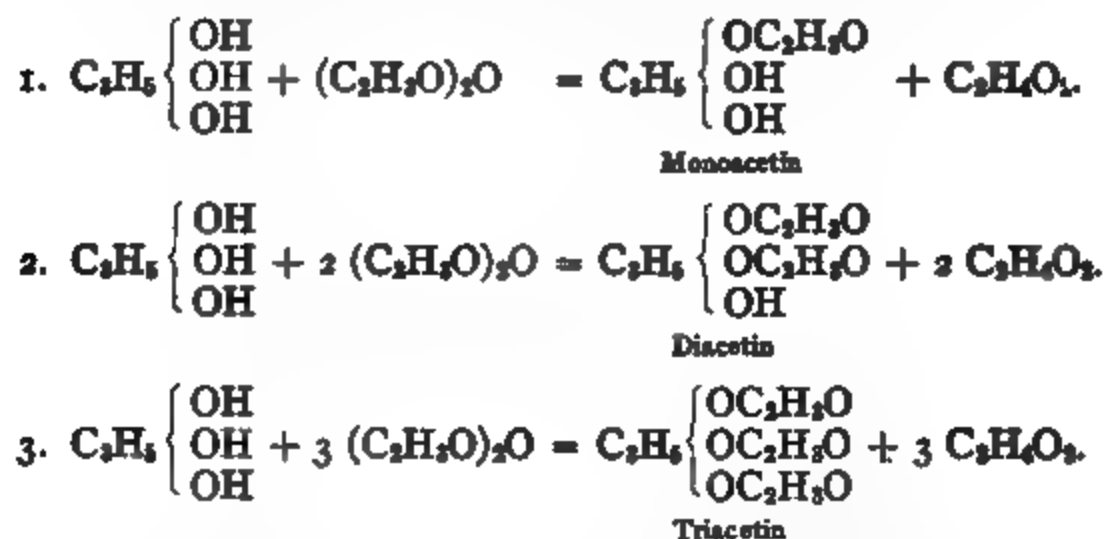
The monochloro and the dichlorohydrins are made by dissolving anhydrous glycerol in glacial acetic acid, saturating with hydrochloric acid gas, heating, and then distilling off the acetic acid. The monochlorohydrin is separated from the dichlorohydrin by fractional distillation in a vacuum. The trichlorohydrin is made by heating the dichlorohydrin with phosphorus pentachloride.

*Monochlorohydrin* is chiefly used for the purpose of making

the dinitrate,  $\text{ClCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{ONO}_2)$ . This is a yellow liquid, (b. p.  $190^\circ\text{--}193^\circ$ ), which does not solidify at  $-25^\circ$  to  $-30^\circ$ . It is therefore added to nitroglycerin to prevent it from solidifying at low temperatures. Monochlorohydrin is also used in organic syntheses.

*Dichlorohydrin* is used as a solvent for shellac, resins (copal), nitrocellulose (celluloid), etc., and in organic syntheses.

(2) Glycerol forms three classes of ethereal salts containing one, two, and three acid residues respectively. For example, with acetic anhydride these reactions take place:—



The last reaction (formation of triacetin) is used for the quantitative determination of glycerol in the commercial product.

Commercial "acetin" is a mixture of mono and diacetin and contains very little triacetin. It is made by boiling glycerol and glacial acetic acid together for 48 hours and distilling off the excess of acetic acid. It is used as a solvent for basic dyes, especially indulins, and for tannin in dyeing cotton.

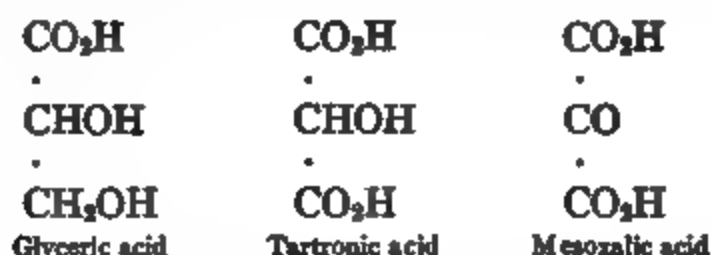
In regard to the relation of the hydroxyl groups to the carbon atoms of the radical  $\text{C}_3\text{H}_5$ , the syntheses of glycerol show that each hydroxyl is in combination with a different

$\text{CH}_2\text{OH}$   
 $\cdot$   
 $\text{CHOH}$ , and, for the  
 $\cdot$   
 $\text{CH}_2\text{OH}$

following additional reasons:

In the first place, it has been shown that compounds containing two hydroxyls in combination with the same carbon atom are unstable. They readily lose water. It would follow from this that the simplest triacid alcohol must contain at least three atoms of carbon, just as the simplest diacid alcohol must contain at least two atoms of carbon. We have seen above that glycerol, the simplest triacid alcohol known, does contain three atoms of carbon.

Further, if the above formula of glycerol is correct, it contains two primary alcohol groups,  $\text{CH}_2\text{OH}$ , and one secondary alcohol group,  $\text{CHOH}$ . Now, it has been shown that the group  $\text{CH}_2\text{OH}$  is converted into carboxyl; and the group  $\text{CHOH}$  into carbonyl  $\text{CO}$  by oxidizing agents. Therefore, we should expect by oxidizing glycerol to get acids having the formulas,—



Products having these formulas actually are obtained by oxidation of glycerol, the first being *glyceric acid* (189) the second *tartronic acid* (192), and the third *mesoxalic acid* (196).

Just as ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , is regarded as water,  $\text{HOH}$ , in which one hydrogen is replaced by the univalent radical  $\text{C}_2\text{H}_5$ ,

and glycol,  $\text{C}_2\text{H}_4$   $\begin{smallmatrix} \text{H} > \text{O} \\ \text{H} > \text{O} \end{smallmatrix}$ , is regarded as two molecules of water in

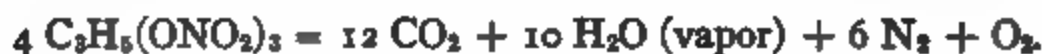
which two hydrogen atoms are replaced by the bivalent radical  $\text{C}_2\text{H}_4$ , so also glycerol may be regarded as three molecules of water in which three hydrogen atoms are replaced by the *tri-valent radical*  $\text{C}_3\text{H}_5$ , thus:—



**Ethereal salts or esters of glycerol.** — Among the important esters of glycerol are the *nitrates*. Several of these are known;

viz., the *mononitrates*,  $C_3H_5 \begin{Bmatrix} ONO_2 \\ OH \\ OH \end{Bmatrix}$ , *dinitrates*,  $C_3H_5 \begin{Bmatrix} ONO_2 \\ ONO_2 \\ OH \end{Bmatrix}$ ,

and the *trinitrate*,  $C_3H_5(ONO_2)_3$ , the latter being the chief constituent of *nitroglycerin*. Nitroglycerin is prepared by adding glycerol *slowly* to a mixture of concentrated sulphuric and nitric acids, the temperature being kept below  $10^\circ$ . It is a pale yellow oil insoluble in water. At low temperatures it crystallizes in long needles. It explodes very violently by concussion. It can be burned in an open vessel, but if heated quickly it explodes. The products of the chemical change that takes place are carbon dioxide, steam, free nitrogen and oxygen which occupy 10,000 times the volume of the nitroglycerin: —



This fact accounts for the enormous explosive power of the substance.

On account of the danger and difficulty of handling it in the liquid state, nitroglycerin as such is used only for special purposes, such as blasting oil wells. Approximately 7,000,000 pounds are used in this manner each year in the United States.

**Dynamite**, introduced by Nobel in 1867, was originally 75 parts of nitroglycerin absorbed in 25 parts of kieselguhr. This made a plastic mass, safe and convenient to handle. Kieselguhr, however, is inert, and produces no gas on explosion of the dynamite. A distinct improvement was made by the substitution for kieselguhr of a mixture of wood flour and a nitrate, such as sodium or potassium nitrate. The dynamites manufactured in America at present are mixtures of this type and contain from 10 per cent to 70 per cent nitroglycerin. No kieselguhr dynamite has been manufactured in the United States since about 1890.

In 1870, Nobel discovered that a small percentage of collodion cotton would cause nitroglycerin to form a stiff jelly. A mix-

ture of 91 per cent nitroglycerin and 9 per cent of this nitrocellulose is called *blasting gelatin*. It is a stiff, plastic jelly, giving only gases on explosion, and is the strongest explosive known.

*Gelignites* and *gelatin dynamites* are prepared by making a thinner jelly — containing lower ratios of nitrocellulose — and incorporating therein a mixture of wood flour and sodium or potassium nitrate.

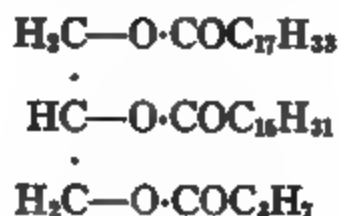
All of these blasting explosives are detonated by means of mercury fulminate.

The annual production in the United States of commercial blasting explosives containing nitroglycerin is approximately 300,000,000 pounds.

In the manufacture of some types of smokeless powder, nitroglycerin is used to gelatinize nitrocellulose. *Cordite* and *ballistite* are the most important of such types. They contain from 30–60 per cent nitroglycerin, and from 35–65 per cent nitrocellulose.

When treated with alkali, nitroglycerin is saponified, yielding glycerol and a nitrate. This shows that it is an ester of nitric acid, and not a nitro compound. ✓

**Fats.** — The natural fats consist almost entirely of the fatty acid esters of glycerol. It has usually been assumed that the fats are simply mixtures of varying amounts of the neutral esters, tripalmitin, tristearin, and triolein, and that the fat is solid, semi-solid, or liquid, according to the amount of olein (which is liquid) present. Recent investigations show that mixed esters, compounds containing different fatty acids combined with the same glycerol molecule, occur much more frequently than had been supposed. Thus oleopalmitobutyrate: —



has been isolated from cow's butter, and other mixed esters of



glycerol have been isolated from beef tallow, lard, cocoa butter and olive oil. Human fat consists mainly of tripalmitin and a dioleostearin. Glycerol is the only polyacid alcohol found in fats.

Fats are very widely distributed in nature, both in plants and animals. They are of the highest importance from the economic and physiological point of view, forming one of the three great classes of foodstuffs.

They are the source of the manufacture of soaps, candles, and glycerol.<sup>1</sup>

In the digestion of fats in the intestines, they are completely hydrolyzed in the alkaline digestive fluids into glycerol and soap by means of an enzyme, *lipase*, present in these fluids. The glycerol and some of the fatty acids are then recombined in the epithelial cells of the intestines, probably by means of the *lipase*, into the fats characteristic of the animal.

Butter consists of mixed esters of glycerol with the following acids: myristic, palmitic, oleic, and stearic acids, which are not volatile, and butyric, caproic, caprylic, and capric acids, which are volatile with steam. *Tributyrim* is not present in butter. All the acids mentioned except oleic acid are members of the fatty acid series. Some of these acids are soluble and some are insoluble in water. The percentage of insoluble fatty acids contained in butter has been found to be about 88 per cent. As the proportion of insoluble fatty acids contained in butter substitutes, which must be labelled *oleomargarin* in the United States, is greater than that contained in butter, it is not a difficult matter to distinguish between the two by determining the amount of these acids contained in them.

Legally in the United States butter must contain 82.5 per cent butter fat of a specific gravity of not less than 0.905 at 40° compared with water at 40° taken as unity. The butter fat must also contain enough volatile fatty acids in a 5 gram sample to neutralize not less than 24 cc. of 0.1-N sodium hydroxide solution (Reichert-Meissl Number).

<sup>1</sup> See *Chemical Technology and Analysis of Oils, Fats and Waxes*, by J. Lewkowitsch, 6th ed., 1921.

## TRIBASIC ACID

**Tricarballic acid,  $C_3H_3(CO_2H)_3$ .** — This acid can be made from trichlorohydrin,  $C_3H_5Cl_3$  (167), by replacing the chlorine by cyanogen, and heating the *tricyanhydrin* thus obtained with a solution of an alkali. It can be made also by treating aconitic acid (295) with nascent hydrogen. It crystallizes from water in orthorhombic prisms that melt at  $162^\circ$ – $164^\circ$ .

## TETRACID ALCOHOLS

**Erythritol, erythrite, butane tetrol 1,2,3,4,  $CH_2OH(CHOH)_2CH_2OH$ .** — This substance occurs free in one of the algae (*Protococcus vulgaris*) and as the ester of orsellinic acid in several lichens. It crystallizes from water in tetragonal prisms. It has a sweet taste. The fact that the simplest tetracid alcohol contains four atoms of carbon, two of which are *asymmetric*, should be specially noted. Erythritol gives secondary butyl iodide with hydriodic acid.

The erythritol occurring in nature is optically inactive. Dextro and levoerythritol, and the inactive mixture of the two are also known. When oxidized it gives erythronic acid,  $CH_2OH(CHOH)_2CO_2H$ , and then mesotartaric acid,  $(CHOH)_2(CO_2H)_2$  (202).

*Tetrabasic acids* derived from the hydrocarbons of the paraffin series have been made, but they are not important.

## PENTACID ALCOHOLS

**Pentane pentol 1,2,3,4,5,  $CH_2OH(CHOH)_3CH_2OH$ .** — One pentacid alcohol, adonitol, occurs in nature in *Adonis vernalis*. It is also formed by the reduction of the pentose, ribose (218), with sodium amalgam. It is soluble in water and in ethyl alcohol, but is insoluble in ether. Its melting point is  $102^\circ$ . The other pentacid alcohols, *xylitol* and *arabitol*, are stereoisomers of adonitol and are obtained by the reduction of the pentoses, xylose and arabinose (217). Dextro, levo, and optically inactive (*dl*) modifications of arabitol are known. From the above formula it will be seen that it contains three asymmetric carbon atoms, one of which is pseudosymmetrical.<sup>1</sup>

**Rhamnitol, hexane pentol 1,2,3,4,5,** obtained by reducing the pentose, rhamnose (218), is a pentacid alcohol containing six carbon atoms. It has the formula  $CH_2OH(CHOH)_4CH_2OH$ , and is optically active. *Rhoditol* and *fucitol* are stereoisomers of rhamnitol.

<sup>1</sup> See *Stereochemistry*, by A. W. Stewart, for explanation of pseudo-symmetry.

These alcohols are closely related to the sugars called pentoses. The pentoses are formed from them by mild oxidation, and they are formed from the pentoses by reduction.

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Pentabasic acids have been made, but they are of no special importance.

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### HEXACID ALCOHOLS

**Hexane hexol 1,2,3,4,5,6,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$ .** — There are several hexacid alcohols known. Most of them are derived from hexane, and have the composition represented by the formula  $\text{C}_6\text{H}_{14}(\text{OH})_6$ . It will be noticed that these *hexacid alcohols* contain *six carbon atoms*, four of which are *asymmetric*. They are closely related to the sugars, mannose, fructose, galactose, and glucose.

**Mannitol, mannite,  $\text{C}_6\text{H}_{14}(\text{OH})_6$ .** — Mannite is very widely distributed in the vegetable kingdom. It occurs most abundantly in manna,<sup>1</sup> which is the partly dried sap of the manna ash (*Fraxinus ornus*), a tree cultivated in Sicily. It is obtained from incisions in the bark of the tree. Mannitol makes up 30 to 60 per cent of manna. It is found also in certain mushrooms, in celery, in olives, in the leaves of *syringa* (mock orange), and in many other plants. It forms 20 per cent of dried *Agaricus integer*.

Mannitol is formed in the lactic acid fermentation of sugar. It is formed also by the action of nascent hydrogen on fructose or mannose. It crystallizes in needles, or rhombic prisms, easily soluble in water and in alcohol. It has a sweet taste.

Nitric acid converts mannitol into *mannosaccharic acid*,  $\text{HOOC}(\text{CHOH})_4\text{COOH}$ , (205). When boiled with concentrated hydriodic acid, it is converted into a mixture of 2-iodo- and 3-iodohexane,  $\text{C}_6\text{H}_{13}\text{I}$ .

**Mannitol hexanitrate, (nitromannite),  $\text{C}_6\text{H}_9(\text{O.NO}_2)_6$ ,** is formed by treating mannitol with a mixture of concentrated sulphuric and nitric acids. It is a solid substance and is very explosive. (Analogy with nitroglycerin.)

<sup>1</sup> The manna of the Scriptures was probably obtained from the branches of *Tamarix gallica*. It contains no mannite, but a fermentable sugar.

**Mannitol hexacetate**,  $C_6H_8(O.C_2H_3O)_6$ , is formed by treating mannitol with *acetic anhydride*. Its formation, as well as that of the hexanitate, shows that mannitol is a hexacid alcohol. *The number of acetyl groups that enter into a compound when it is treated with acetic anhydride shows how many hydroxyl groups are in the compound.*

There are three varieties of mannitol — *dextromannitol*, *levomannitol*, and a mixture of the two known as *inactive mannitol*, or *a-acritol*.

**Dulcitol**,  $C_6H_8(OH)_6$ . — This alcohol occurs in a kind of manna obtained from Madagascar, the source of which, however, is unknown. It is formed by treating sugar of milk or galactose with nascent hydrogen.

Nitric acid oxidizes dulcitol, forming mucic acid (206),  $HOOC(CHOH)_4COOH$ , stereoisomeric with mannosaccharic acid. Like mannitol, when boiled with hydriodic acid, it yields a mixture of 2-iodo- and 3-iodohexane,  $C_6H_{13}I$ .

**Sorbitol**,  $C_6H_8(OH)_6 + H_2O$ . — Ordinary sorbitol occurs in the ripening berries of the mountain ash (*Sorbus aucuparia*), and other fruits, as plums, cherries, apples, etc. It is formed by reduction of glucose and also, together with mannitol, by the reduction of fructose. This variety is known as *d'*-sorbitol because it is formed from glucose, which is dextrorotatory. *l'*-Sorbitol is also known, having been obtained by the reduction of levoglucose. Sorbose bacteria convert *d'*-sorbitol into *d'*-sorbose (234).

Mannitol, sorbitol, and dulcitol are stereoisomers. *Talitol* and *iditol* are stereoisomers of mannitol, dulcitol, and sorbitol.

There are *hexabasic acids* known belonging to this series, but they are not important.

#### HEPTACID ALCOHOLS, ETC.

**Perseitol**,  $C_7H_{14}(OH)_7$ , occurs in the fruit, seeds, and leaves of *Laurus persea*, and has been made synthetically from *dextromannose* by treating it with hydrocyanic acid, hydrolyzing the nitrile obtained, and reducing the lactone of the acid thus formed. It is also called *dextromannoheptitol*. By similar reactions an octacid alcohol and an alcohol with nine hydroxyls have also been made from glucose.

## CHAPTER X

### MIXED COMPOUNDS — DERIVATIVES OF THE PARAFFINS

UNDER this head are included compounds that belong at the same time to two or more of the chief classes already studied. Thus, there are substances that are at the same time alcohols and acids. There are others that are at the same time alcohols and aldehydes, alcohols and ketones, acids and ketones, etc. Among them are many of the most important natural compounds of carbon. The first class that presents itself is that of the *alcohol acids* or *acid alcohols*; that is, substances that combine within themselves the properties of both alcohol and acid. They are the *oxy acids* or *hydroxy acids*.

#### HYDROXY ACIDS, $C_nH_{2n}O_3$



These acids may be regarded either as monobasic acids into which one alcoholic hydroxyl has been introduced, or as mon-acid alcohols into which one carboxyl has been introduced. As their acid properties are more prominent than the alcoholic properties, they are commonly referred to the acids. Running parallel, then, to the series of fatty acids, we may look for a series of hydroxy acids, each of which differs from the corresponding fatty acid by one atom of oxygen, or by containing one hydroxyl in the place of one hydrogen, thus: —

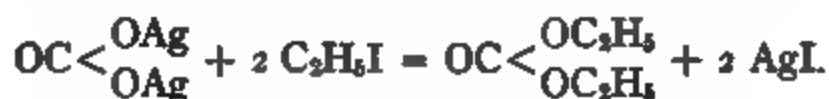
FATTY ACIDS			HYDROXY ACIDS		
$H.CO_2H$	Formic	Acid	$HO.CO_2H$	Carbonic	Acid.
$CH_3.CO_2H$	Acetic	"	$CH_2 \begin{smallmatrix} OH \\ CO_2H \end{smallmatrix}$	Glycolic	"
$C_2H_5.CO_2H$	Propionic	"	$C_2H_4 \begin{smallmatrix} OH \\ CO_2H \end{smallmatrix}$	Lactic	"
etc.			etc.		

The first member of the series, which by analogy would be called *hydroxyformic acid*, is plainly the ordinary hypothetical carbonic acid. Although its relation to formic acid is the same as that of the next member of the series to acetic acid, it has no properties in common with the alcohols; but, owing to its structure, it is a dibasic acid, while the other members of the series are not. Nevertheless, it may be referred to here for the sake of a few of its derivatives, which are somewhat allied to those of the hydroxy acids.

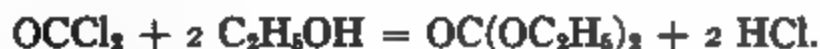
Carbonic acid,  $\text{H}_2\text{CO}_2$ ,  $\text{OC} < \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$  — It is believed that this compound exists in solutions of carbon dioxide in water. When this solution is treated with zinc dust hydrogen is evolved and zinc carbonate is formed. It is a feeble dibasic acid, and breaks down into water and carbon dioxide whenever it is set free from its salts. We have seen that this instability is characteristic of compounds containing two hydroxyls in combination with the same carbon atom.

Among the derivatives of carbonic acid that should be mentioned here are the ethereal salts. These may be made:—

1. By heating silver carbonate with alkyl iodides; as, for example:—



2. By heating the alcohols or sodium alcoholates with carbonyl chloride,  $\text{OCCl}_2$ :—



Carbonyl chloride, phosgene,  $\text{OCCl}_2$ , is the chloride of carbonic acid. It was first obtained by the direct union of carbon monoxide and chlorine in the sunlight, hence the name phosgene (Gr. *phos*, light; Gr. *gennas*, I produce). It results also from the oxidation of chloroform (27) and from the action of fuming sulphuric acid (80 per cent  $\text{SO}_3$ ) on carbon tetrachloride:—



It is most conveniently prepared in the laboratory by the last method. Technically it is made by conducting carbon monoxide and chlorine over some catalytic agent (bone black). It is a colorless gas with a suffocating odor. It is readily condensed to a liquid below  $8^{\circ}$ . It is very soluble in benzene and toluene. It is poisonous. As an acid chloride it is hydrolyzed by water into carbon dioxide and hydrochloric acid. It hence reacts with acids abstracting water and forming acid anhydrides. It converts aldehyde into ethylidene chloride : —



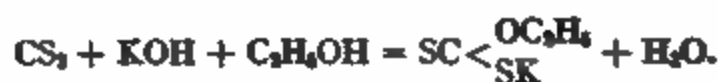
With ammonia it gives urea (262). Large quantities are used in making dyes, intermediates, and in synthetic work. It was used as a "poison gas" during the World War.

Ethyl chlorocarbonate,  $\text{OC} \begin{smallmatrix} \text{Cl} \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$ , boils at  $93^{\circ}$  and acts as an acid chloride and as an ester, *e.g.* it is hydrolyzed by water to hydrochloric acid and ethyl hydrogen carbonate, which is unstable and breaks down into carbon dioxide and alcohol. It is largely used in synthetic work and for the purpose of introducing the carboxyl group into compounds.

It may be regarded as the ethyl ester of monochloroformic acid,  $\text{Cl}.\text{COOH}$ ; and, properly speaking, should be called *ethyl chloroformate*.

Carbon bisulphide acts like carbon dioxide towards alkalis and alcohols, and yields a number of ether acids and ethereal salts containing sulphur. Thus, when carbon bisulphide is added to a solution of caustic potash in alcohol, a potassium salt of the formula  $\text{SC} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{SK} \end{smallmatrix}$  is formed.

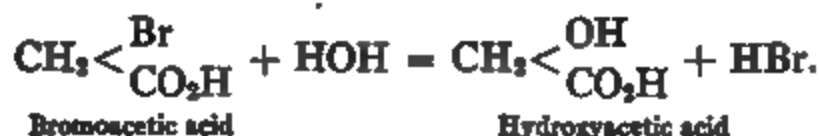
This is called *potassium xanthate*. Free xanthic acid is very unstable, breaking down into alcohol and carbon bisulphide. The formation of the salt is represented thus :—



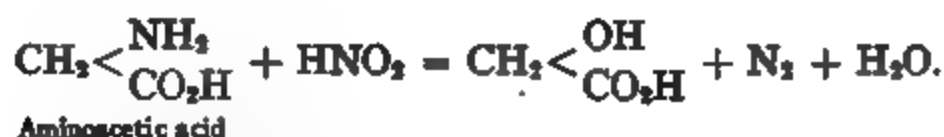
A similar salt made from ordinary amyl alcohol has been used for the purpose of destroying *phylloxera*, the insect that is so destructive to grapevines, particularly in the wine districts of France.

*General methods for the preparation of hydroxy acids:—*

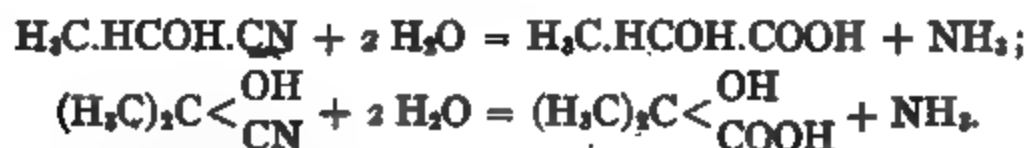
1. Heating a halogen derivative of an acid with water or silver hydroxide:—



2. By treating an *amino derivative* of an acid with nitrous acid (105):—

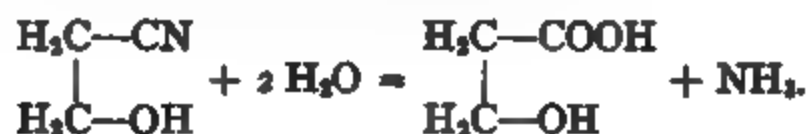


3. From aldehydes or ketones by first converting them into the cyanhydrins by the action of hydrocyanic acid, and hydrolyzing the latter:—



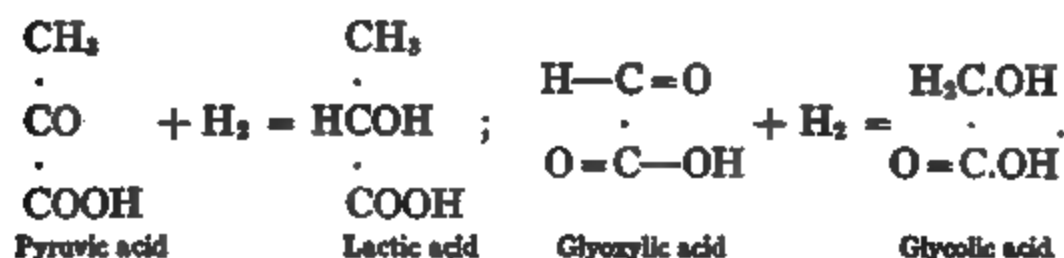
As the aldehydes and ketones are readily made from the primary and secondary alcohols by oxidation, this is an indirect method of introducing carboxyl into the alcohols in place of hydrogen. This method always gives an  $\alpha$ -hydroxy acid.

4. By hydrolysis of glycol cyanhydrin, made from ethylene chlorohydrin (152):—



This method gives a  $\beta$ -hydroxy acid.

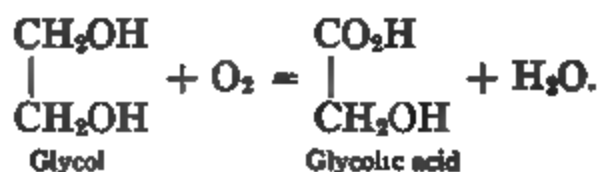
5. By the reduction of aldehyde or ketone acids:—





**Glycolic acid, hydroxyacetic acid, oxyacetic acid, ethanol acid,  $C_2H_4O_3$ ,  $CH_2<\begin{smallmatrix} OH \\ CO_2H \end{smallmatrix}$ .** — Glycolic acid is found in nature in unripe grapes, and in the leaves of the wild grape (*Ampelopsis hederacea*).

It can be made from glycocoll, which is aminoacetic acid (see reaction 2, above), from bromo or chloroacetic acid and water (see reaction 1, above), and by the oxidation of glycol: —



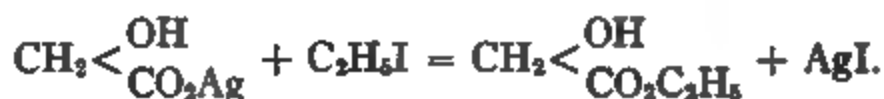
This results in transforming one of the primary alcohol groups,  $CH_2OH$ , contained in glycol, into carboxyl.

NOTE FOR STUDENT. — What would be formed by conversion of both the primary alcohol groups of glycol into carboxyl?

It can also be made by careful oxidation of ethyl alcohol with nitric acid. For this purpose a mixture of alcohol and nitric acid is allowed to stand until no further action takes place. Glycolic acid crystallizes from the solution on evaporation.

Glycolic acid forms crystals that are easily soluble in water, alcohol, and ether. It melts at  $80^\circ$ . It is a very much stronger acid than acetic acid.

As an acid, glycolic acid forms a series of salts with metals, and ethereal salts with alcohol radicals. The latter, of which ethyl glycolate may be taken as an example, can be made by means of one of the reactions usually employed for making ethereal salts; for example, by treating silver glycolate with ethyl iodide: —

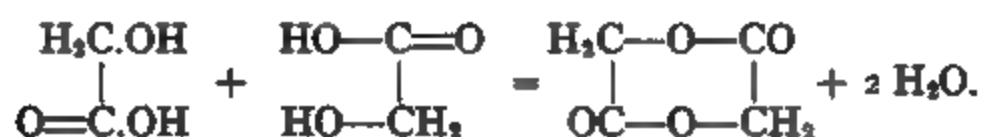


In this reaction, as well as in the formation of salts of glycolic acid, the alcoholic hydroxyl remains unchanged.

As an alcohol, glycolic acid forms ethers of which *ethylglycolic acid*,  $\text{CH}_2 < \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{CO}_2\text{H} \end{smallmatrix}$ , may serve as an example. It will be seen that this is isomeric with ethyl glycolate. But while the latter has alcoholic properties, the former has acid properties. Ethyl glycolate is a liquid that boils at  $160^\circ$ . Ethylglycolic acid is a liquid that boils at  $206^\circ$  to  $207^\circ$ . Finally, as an alcohol, glycolic acid forms ethereal salts, of which acetylglycolic acid may serve as an example. This is glycolic acid in which the hydrogen of the hydroxyl is replaced by acetyl,  $\text{CH}_2 < \begin{smallmatrix} \text{O.C}_2\text{H}_5\text{O} \\ \text{CO}_2\text{H} \end{smallmatrix}$ . As will be seen, this bears the same relation to glycolic acid and acetic acid that ethyl acetate,  $\text{C}_2\text{H}_5.\text{O.C}_2\text{H}_3\text{O}$ , bears to alcohol and acetic acid.

Glycolic acid and some of the other acids of the series lose water when heated, and yield anhydrides. Thus *glycolic anhydride*,  $\begin{smallmatrix} \text{H}_2\text{COH} \\ | \\ \text{OC}-\text{OCH}_2\text{COOH} \end{smallmatrix}$ , is formed when glycolic acid is heated to  $100^\circ$ . This substance is plainly an ester, an alcohol, and an acid.

When glycolic acid is distilled in a vacuum it yields *glycolide*, which is derived from the acid as represented in this equation:—

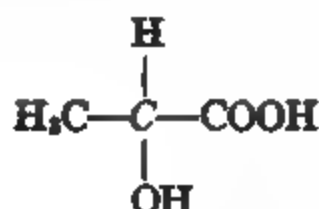


It is a double ester resulting from the interaction of the alcoholic hydroxyl of each molecule of the glycolic acid with the carboxyl of the other.

Glycolide is insoluble in cold water. When boiled for a long time with water, it is converted into glycolic acid. It melts at  $87^\circ$ .

**Lactic acids, hydroxypropionic acids, oxypropionic acids,**  $\text{C}_3\text{H}_5\text{O}_3$ ,  $\text{C}_3\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{CO}_2\text{H} \end{smallmatrix}$ .—In treating of propionic acid, it was pointed out that two series of mono substitution products

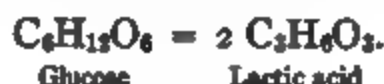
of the acid are known, which are designated as the  $\alpha$ - and  $\beta$ -series. Accordingly we should expect to find two hydroxypropionic acids, the  $\alpha$ - and the  $\beta$ -acid, and both are known. The  $\alpha$ -hydroxypropionic acids or lactic acids contain an asymmetric carbon atom: —



and the dextro, levo, and inactive (*dl*) forms predicted by the theory (see active Amyl alcohols, 137) are all known.

$\beta$ -Hydroxypropionic, hydracrylic acid,  $\text{HOH}_2\text{C}.\text{CH}_2.\text{COOH}$ , does not contain an asymmetric carbon atom and is only known in one form, which, of course, is optically inactive.

1. Lactic acid, inactive ethylenelactic acid,  $\alpha$ -hydroxypropionic acid, propanol-2-acid,  $\text{H}_2\text{C}.\text{CHOH}.\text{COOH}$ . — This acid is formed in the lactic acid fermentation of milk sugar, cane sugar, or glucose and is hence called fermentation lactic acid. It can also be obtained from the carbohydrates by the action of alkalies. From 50 to 60 per cent of glucose or fructose can be converted in this way into inactive lactic acid: —



With certain lactic acid bacteria over 98 per cent of glucose can be converted into inactive *dl*-lactic acid. This microorganism is extremely sensitive to the free acid, and hence the fermentation is brought about in the presence of calcium or zinc carbonate to neutralize the free acid as fast as it is formed. The lactic acid is afterwards set free from these salts by means of sulphuric acid.

As in the case of the fermentation of glucose to alcohol (39, 40) the formation of lactic acid from sugar is caused by an enzyme produced by the microorganism. This lactic acid fermentation plays a very important part in many practical processes, as in butter-making, when the cream is allowed to become sour

before churning, or a "starter" (lactic acid ferment) is added to it; in the ripening of cheese; in the fermentation of cabbage in making sauerkraut; and in the change of cucumbers into dill pickles. Silage, used largely as a cattle food, contains large quantities of lactic acid. Lactic acid is also present in small quantity in wines and in opium. That lactic acid is  $\alpha$ -hydroxypropionic acid follows from its formation from  $\alpha$ -chloro- and  $\alpha$ -bromopropionic acids by heating with solutions of the alkalies, from pyruvic acid by reduction (see method 5, 179), and from aldehyde (see method 3, 179). The inactive *dl*-lactic acid always results from these chemical methods of preparation. Lactic acid was first isolated from sour milk and hence its name (*lac*, milk).

Commercial lactic acid is a thick, hygroscopic syrup, sp. gr. 1.21-1.22, that contains about 80 per cent acid. It mixes with water and alcohol in all proportions and can be extracted from its aqueous solutions by means of ether. When purified by distillation in a *vacuum*, lactic acid forms crystals that melt at 18°. The zinc salt of the inactive *dl*-acid crystallizes with 3 molecules of water of crystallization, while the zinc salts of both the dextro and the levo acid contain only 2 molecules of water of crystallization. The zinc salts of the two active acids are also much more soluble in water than that of the inactive *dl*-acid. Hence when equal amounts of these salts are dissolved in water, the zinc salt of the inactive *dl*-acid with 3 molecules of water crystallizes out of the solution. Heated with hydriodic acid all the lactic acids are reduced to propionic acid:—



This shows that the isomerism is due to the asymmetric carbon atom as it disappears with the asymmetric carbon atom. With hydrobromic acid lactic acid gives  $\alpha$ -bromopropionic acid:—



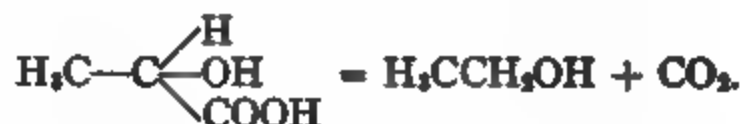
and the *d*-, *l*-, and *dl*-varieties of this acid are all known, as it still contains the asymmetric carbon atom.

The lactic acid obtained by the fermentation of the carbohydrates is almost always the inactive *dl*-variety. Systematic investigation has shown that it depends essentially on the nature of the microorganism and the conditions as to whether the inactive (*dl*) or active acid is obtained. Seldom is the dextro or levo form obtained alone; generally the inactive acid is formed with a slight excess of the *d*- or the *l*-acid.

Lactic acid has been identified as an intermediate product in the alcoholic fermentation of glucose:—



It has been suggested that it then gives ethyl alcohol by the loss of carbon dioxide:—



The objection to this suggestion, however, is that lactic acid is not converted into alcohol and carbon dioxide by fermentation with yeast.

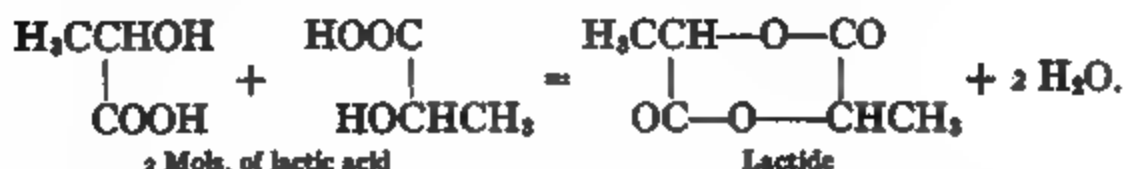
Lactic acid is used as a mordant in dyeing, especially in the form of its antimony compound; in the leather industry to remove lime and the calcium salts of the fatty acids from the skins after they have been dehaired in the lime-vat; and in the form of its compound with titanous acid in the manufacture of leather. It is also used in the manufacture of alcohol (to prevent the growth of other organisms than yeast). Several salts of lactic acid are used in medicine.

When heated with dilute sulphuric acid, lactic acid gives acetic aldehyde and formic acid:—



This reaction, which is characteristic of the  $\alpha$ -hydroxy acids, is used as a test for lactic acid. When oxidized *all* the lactic acids give pyruvic acid,  $\text{CH}_3.\text{CO}.\text{COOH}$  (207), and this proves the presence of the secondary alcohol group in lactic acid. It

will be noted that pyruvic acid does not contain an asymmetric carbon atom. When lactic acid is distilled in a vacuum, lactide, a double ester analogous to glycolide, results:—



This forms colorless plates melting at  $120^\circ$ . It is insoluble in water, but is converted into lactic acid by boiling with water.

2. **Sarcolactic acid, dextrolactic acid,  $\text{H}_3\text{C}.\text{CHOH}.\text{COOH}$ ,** occurs in the liquid expressed from meat, whence its name. It is therefore most readily obtained from the extract of meat. It crystallizes in prisms, melting at  $25^\circ\text{--}26^\circ$  and is extraordinarily hygroscopic. It resembles the inactive *dl*-acid very closely in its properties and in its conduct towards reagents, but while the fermentation lactic acid is optically inactive, this lactic acid is *dextrorotatory*. Its salts and esters are *levorotatory*.

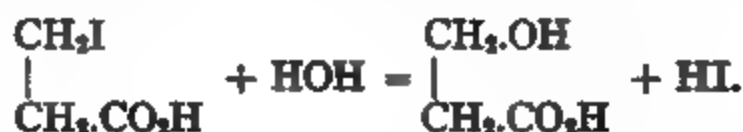
3. **Levolactic acid,  $\text{CH}_3.\text{CHOH}.\text{COOH}$ .**—This second optically active modification of lactic acid was first obtained by fermenting cane sugar with the levolactic acid bacillus. It turns the plane of polarized light to the *left*, the same number of degrees that sarcolactic acid turns it to the *right*, while its salts and esters are *dextrorotatory*. Its other physical properties, such as melting point, solubility, crystal system, etc., are the same as those of sarcolactic acid, in accordance with the stereochemical theory.

Both optically active forms have been obtained from the inactive *dl*-lactic acid by the use of the proper microorganisms, one organism destroying one form and another organism the opposite variety. Another method that has been used for this purpose is fractional crystallization of the strychnine salt of the inactive *dl*-acid. Strychnine is a levorotatory base, hence there are two salts (*d*-acid-*l*-base and *l*-acid-*l*-base). These two salts are not mirror images and have different solubilities. The strychnine salt of the levo acid (*l*-acid-*l*-base) is less soluble and crystallizes out first. By precipitating the

strychnine with ammonia the ammonium salts of the active acids are obtained from the strychnine salts.

The lactic acids are very much stronger acids than propionic acid and much stronger than hydracrylic acid.

4. **Hydracrylic acid,  $\beta$ -hydroxypropionic acid, propanol-3-acid,  $\text{CH}_2\text{OHCH}_2\text{CO}_2\text{H}$ .**—Hydracrylic acid is made by boiling  $\beta$ -iodopropionic acid with water or silver oxide and water:—



It is made also by starting with ethylene,  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$ . When this is treated with hypochlorous acid,  $\text{HOCl}$ , it is converted into ethylene chlorhydrin,  $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CH}_2\text{OH} \end{array}$  (152). By substituting cyanogen

for chlorine and boiling the cyanhydrin,  $\begin{array}{c} \text{CH}_2\text{CN} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , thus obtained with an alkali, hydracrylic acid is obtained.

These reactions clearly show that hydracrylic acid is an ethylene compound, and as it is made from  $\beta$ -iodopropionic acid by replacing the iodine with hydroxyl, it follows further that the  $\beta$ -substitution products of propionic acid are ethylene compounds, and that the  $\alpha$ -products are ethylidene compounds (145). When oxidized, hydracrylic acid gives malonic acid,  $\text{CH}_2(\text{COOH})_2$ . This proves the presence of the primary alcohol group. With hydriodic acid it gives  $\beta$ -iodopropionic acid.

Hydracrylic acid is a syrup. Its salts differ markedly from those of the inactive and active lactic acids. When heated, it loses water and is transformed into *acrylic acid*,  $\text{CH}_2:\text{CH}.\text{CO}_2\text{H}$  (286); and acrylic acid when heated with a solution of sodium hydroxide gives sodium hydracrylate:—

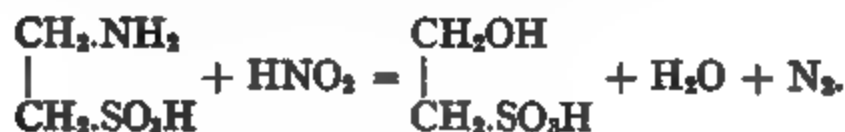


The difference in conduct between ethylidenelactic acid and hydracrylic acid, when heated, is interesting and suggestive.

When ethylidenelactic acid is heated it gives lactide. Both the alcoholic and acid hydroxyls take part in the reaction. Whereas, when ethylenelactic acid is heated, only the alcoholic properties are destroyed, the carboxyl remaining intact.

**Hydroxysulphonic acids.** — It has been pointed out that the sulphonic acids and the carboxylic acids are analogous; that, for example, methylsulphonic acid,  $\text{CH}_3\text{SO}_3\text{H}$ , is analogous to methylcarboxylic or acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ . Now, just as the hydroxy acids already treated of are derived from the carboxylic acids by the introduction of hydroxyl, so there are hydroxy acids derived in a similar way from the sulphonic acids. Only one such acid is well known. It is —

**Isethionic acid, ethane-2-ol-1-sulphonic acid,**  $\begin{array}{c} \text{H}_2\text{COH} \\ | \\ \text{H}_2\text{CSO}_3\text{OH} \end{array}$ , also called  *$\beta$ -hydroxyethylsulphonic acid*. It is analogous to hydroacrylic acid. It is prepared by passing sulphur trioxide into well-cooled alcohol or ether and boiling the product with water; and also by treating taurine (254) with nitrous acid: —



When oxidized isethionic acid gives sulphoacetic acid,  $\text{H}_2\text{C} < \begin{array}{c} \text{COOH} \\ \text{SO}_3\text{H} \end{array}$ . This proves its structure. It is isomeric with ethylsulphuric acid,  $\text{C}_2\text{H}_5\text{HSO}_4$ , and is distinguished from this by the fact that the sulphonic acid group is not removed by boiling with water.

**NOTE FOR STUDENT.** — What is formed when ethylsulphuric acid is boiled with water?

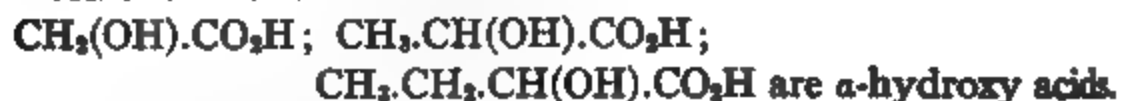
## LACTONES

The monohydroxy monobasic acids of the paraffin series are designated as  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, etc., hydroxy acids, according to the position of the hydroxyl with reference to the carboxyl. When the hydroxyl is united with the carbon atom with which the carboxyl is united, the product is called an  $\alpha$ -hydroxy acid. When



the hydroxyl is united with the next carbon atom in the chain, the product is called a  $\beta$ -hydroxy acid, etc. The following examples will make this clear: —

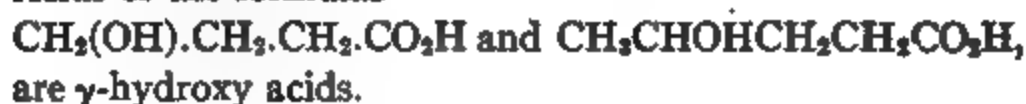
Acids of the formulas



Acids of the formulas



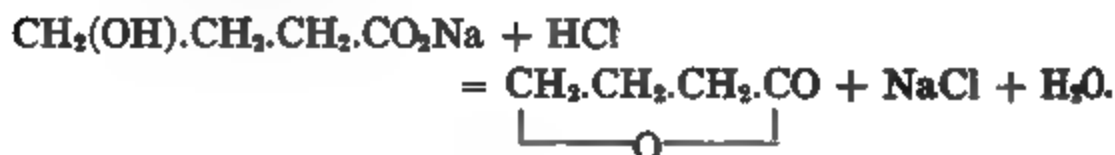
Acids of the formulas



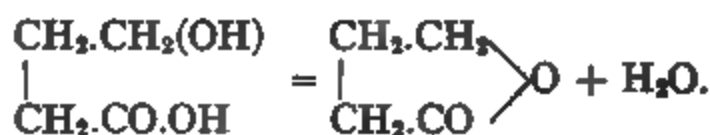
Similarly, an acid of the formula



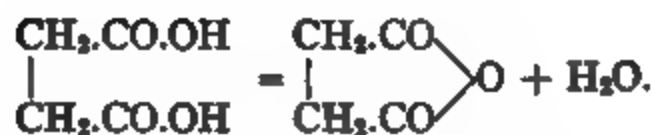
The  $\gamma$ - and  $\delta$ -acids differ from the others in this respect that they lose the elements of water when set free from their salts. Thus, when a salt of  $\gamma$ -hydroxybutyric acid in solution is treated with a mineral acid, a neutral compound is precipitated and not the acid corresponding to the salt. The compound thus formed is called a *lactone*. The reaction between sodium  $\gamma$ -hydroxybutyrate and hydrochloric acid is represented by the following equation: —



The change from the free acid to the lactone may be represented thus: —



The reaction is similar to that which takes place when succinic acid is heated: —

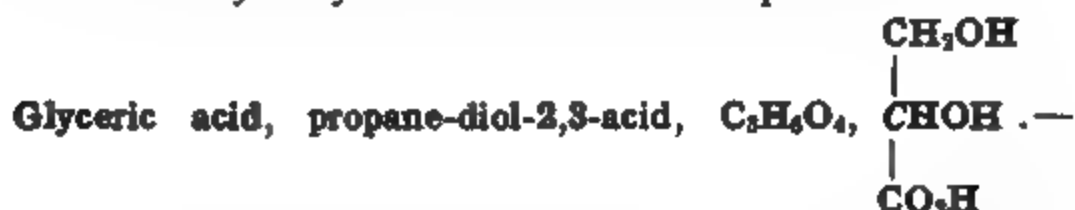


The product in this case is an anhydride. The lactones may be defined as anhydrides of hydroxy acids or better as inner esters. They are neutral, but they form salts of the corresponding hydroxy acids when they are boiled for some time with bases in solution (saponification of the inner ester).

The ease with which *five-* or *six-*membered rings are formed is a characteristic property of carbon compounds.<sup>1</sup> It is due to the tetrahedral arrangement of the atoms around the carbon atoms.

#### HYDROXY ACIDS, $\text{C}_n\text{H}_{2n}\text{O}_4$

The acids just treated of are *monohydroxy monobasic acids*. Similarly, there are *dihydroxy monobasic acids*, which are derived from the monohydroxy acids by the introduction of a second hydroxyl. Thus, if into lactic acid,  $\text{CH}_3\text{CHOHCO}_2\text{H}$ , a hydroxyl should be introduced into the methyl, the product would have the formula  $\text{CH}_2\text{OHCHOHCO}_2\text{H}$ . This is the best known dihydroxy monobasic acid of the paraffin series.



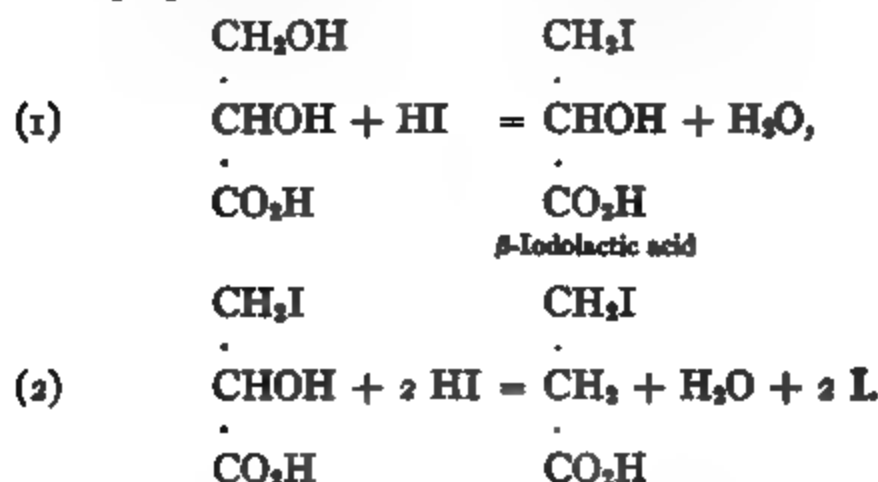
This acid has been referred to as the first product of the oxidation of glycerol. It is prepared by allowing glycerol and fuming nitric acid to stand together at ordinary temperature for some time, and then evaporating on the water bath. It can also be made by treating  $\beta$ -chlorolactic acid (made by the oxidation of monochlorohydrin) with water. It is optically inactive.

Both optically active varieties of glyceric acid have been obtained from the inactive variety by the methods used to

<sup>1</sup> See *Stereochemistry*, by A. W. Stewart, for the explanation of this remarkable property of the carbon atoms.

resolve inactive lactic acid into *d*- and *l*-lactic acids. It will be seen that the acid contains an asymmetric carbon atom.

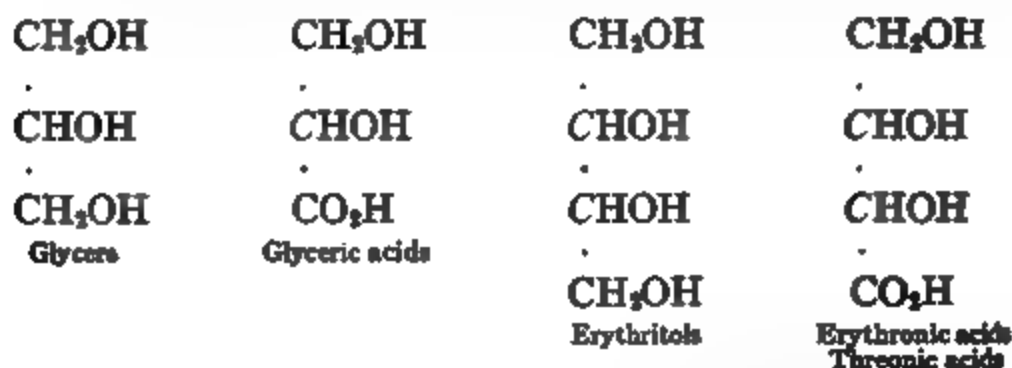
Glyceric acid is a thick syrup that mixes with water and alcohol, but is insoluble in ether. When treated with concentrated hydriodic acid and phosphorus, it is converted into *β*-iodopropionic acid. This conversion involves two reactions:—



*β*-Iodopropionic acid (3-iodopropane acid) melts at 82°, is readily soluble in hot water, but difficultly soluble in cold water. It is frequently used in organic syntheses.

#### OTHER HYDROXY MONOBASIC ACIDS

Just as a dihydroxy monobasic acid is formed by oxidation of the triacid alcohol, glycerol, so by oxidation of the tetraacid alcohols, erythritols, trihydroxy monobasic acids are formed. These are the *erythronic* and *threonic acids*. Their relation to the erythritols is like that of the glyceric acids to glycerol:—

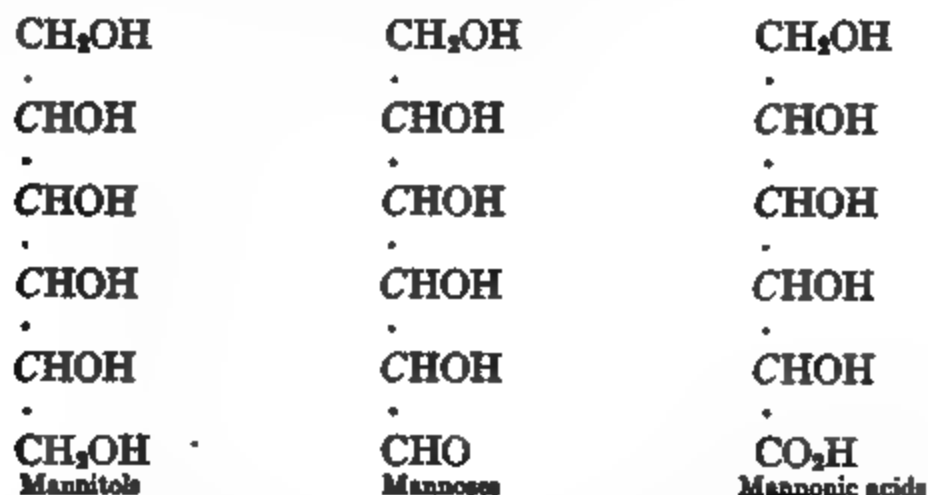


*d*- and *l*-Erythronic acids and the inactive *dl*-form and *d*- and *l*- and *dl*-threonic acids are known. The formula contains two asymmetric carbon atoms, and four stereoisomers are possible.

Similarly, corresponding to the pentacid alcohols, adonitol, arabitol, and xylitol, stereoisomeric tetrahydroxy monobasic acids having the same structural formula,  $\text{H}_2\text{COH}(\text{HCOH})_3\text{COOH}$ , are known. As these acids contain *three* asymmetric carbon atoms; eight optically active stereoisomers (four *d*- and four *l*- forms) and four optically inactive *dl*-forms are theoretically possible. They are known as arabonic, ribonic, xylonic, and lyxonic acids from the fact that they are made by the oxidation of the sugars (pentoses), arabinose, ribose, xylose, and lyxose. Dextro-, levo-, and inactive (*dl*) forms of all these acids are known.

Pentahydroxy monobasic acids are also known and are of special importance on account of their connection with the most important sugars, the hexoses. They are made from the aldopentoses by the cyanhydrin reaction and from the aldohexoses by oxidation.

**Mannonic acids**,  $\text{C}_6\text{H}_{12}\text{O}_7[\text{C}_6\text{H}_5(\text{OH})_5\text{CO}_2\text{H}]$ . — Three acids are included in this group. They are the *dextro*, the *levo*, and the *inactive (dl)* varieties, or *d-mannonic*, *l-mannonic*, *dl-mannonic acids*. They are related to the three mannitols and the three mannoses. As will be shown farther on, the mannoses are pentahydroxy aldehydes, and the relations here referred to are represented by the following formulas:—



The difference between the three mannonic acids is of the same kind as that between the three lactic acids. The dextro and levo varieties are optical antipodes, while the inactive form is a combination of the dextro and levo varieties.

**Gluconic acids**,  $\text{C}_6\text{H}_{12}\text{O}_7[\text{C}_6\text{H}_5(\text{OH})_5\text{CO}_2\text{H}]$ . — The three gluconic acids are related to the three glucoses in the same way that the mannonic acids are related to the mannoses. *Dextro*-

*gluconic acid* is formed by the oxidation of *d*-glucose and of cane sugar. When heated with quinoline to  $140^{\circ}$ , it is partly converted into *d*-mannonic acid. Similarly *d*-mannonic acid is partly converted into *d*-gluconic acid by the same process. Three *gulonic acids*, three *galactonic acids*, and *idonic* and *talonic acids* of the same composition and structure as the mannonic and the gluconic acids are also known.

The existence of so many acids of the formula



is due to the fact that it contains four asymmetric carbon atoms and the groups at the end of the chain are different. The total number of isomers possible, according to the stereochemical theory is twenty-four — eight dextro and eight levo, besides eight racemic (*dl*) forms.

#### HYDROXY ACIDS, $\text{C}_n\text{H}_{2n-2}\text{O}_5$

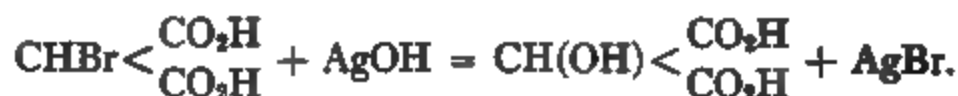
The acids included under this head are *monohydroxy dibasic acids*. They bear the same relation to the dibasic acids of the oxalic acid series that the simplest hydroxy acids bear to the members of the formic acid series. The principal members of this series, and the only ones that will be treated of, are tartronic acid and the malic acids.

**Tartronic acid, propanol diacid,**



— This acid was first obtained from tartaric acid and hence the name. It can be made:—

(1) By boiling bromomalonic acid with silver oxide and water:—



(2) By heating bromocyanacetic acid with a solution of caustic potash:—



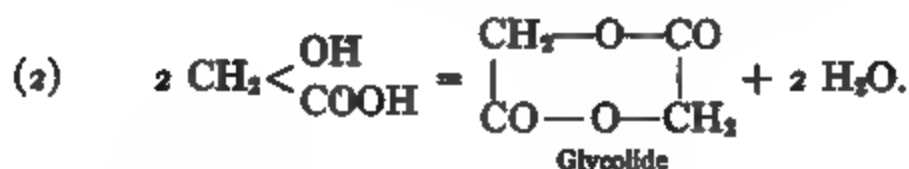
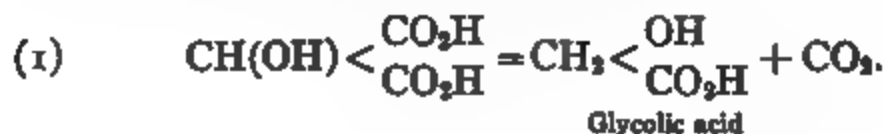
MALIC ACID



193

The bromocyanacetic acid is made by heating dibromoacetic acid with an alcoholic solution of potassium cyanide.

Tartronic acid crystallizes in prisms with a half molecule of water of crystallization. It is easily soluble in water, alcohol, and ether. The anhydrous acid melts at 185–187° with evolution of carbon dioxide and water, and forms glycolide (181):—



NOTE FOR STUDENT.— Compare reaction (1) with that which takes place when isosuccinic acid is heated.

Tartronic acid is also formed by the oxidation of glycerol and by the reduction of mesoxalic acid. On oxidation it gives mesoxalic acid,  $OC(COOH)_2$ , a proof of the presence of the secondary alcohol group.

**Hydroxysuccinic acids,  $HOOC.CHOH.CH_2.COOH$ .**— There is only one monohydroxy succinic acid possible structurally, but, as will be seen from the above formula, it contains an asymmetric carbon atom and dextro-, levo-, and inactive (*dl*) forms are possible and all are known. They are called malic acids (*malum*, apple).



widely distributed in the vegetable kingdom, as in the unripe berries of the mountain ash, in apples, cherries, etc.

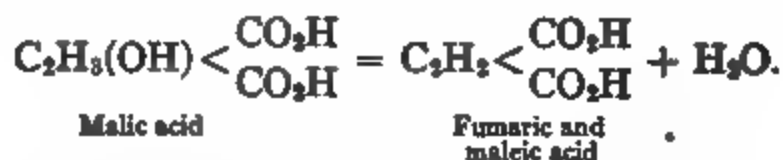
It is present in the sap of the sugar maple as the neutral calcium salt, and this separates, when the sap is evaporated to a syrup, as a granular, sandy precipitate. Hence it is called "sugar sand." The same insoluble neutral calcium salt is formed when the juice of the berries of the mountain ash is boiled with milk of lime. In order to prepare malic acid from

this salt, it is first treated with exactly the right amount of oxalic acid to convert it into the soluble calcium acid malate, and this, after filtering off the calcium oxalate, is crystallized from the solution and purified by recrystallization. The *pure* calcium acid malate is then decomposed in aqueous solution with the exact amount of oxalic acid necessary to precipitate all the calcium, the solution filtered and evaporated on the water bath.

It can also be made by treating aspartic acid, which is amino-succinic acid,  $\text{HOOC.H}_2\text{C.CH(NH}_2\text{)CO}_2\text{H}$ , with nitrous acid, and by treating *l*-tartaric acid with hydriodic acid.

Malic acid crystallizes in needles. It melts at  $100^\circ$ . It is very easily soluble in water and in alcohol, but only slightly soluble in ether. The dilute aqueous solutions are *levorotatory*. A 34 per cent solution is optically inactive at  $20^\circ$ . More concentrated solutions are *dextrorotatory*.

When heated, it loses water and yields fumaric acid and maleic anhydride (290). Fumaric and maleic acids are stereoisomeric, and both are represented by the formula  $\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$ . The reaction mentioned is represented by the following equation: —



NOTE FOR STUDENT. — Compare this reaction with that which takes place when hydracrylic acid is heated.

When boiled with hydriodic acid, *all* the malic acids are reduced to succinic acid.

NOTE FOR STUDENT. — Compare this reaction with the conduct of lactic and glyceric acids when treated with hydriodic acid.

Treated with hydrobromic acid, malic acid is converted into monobromosuccinic acid.

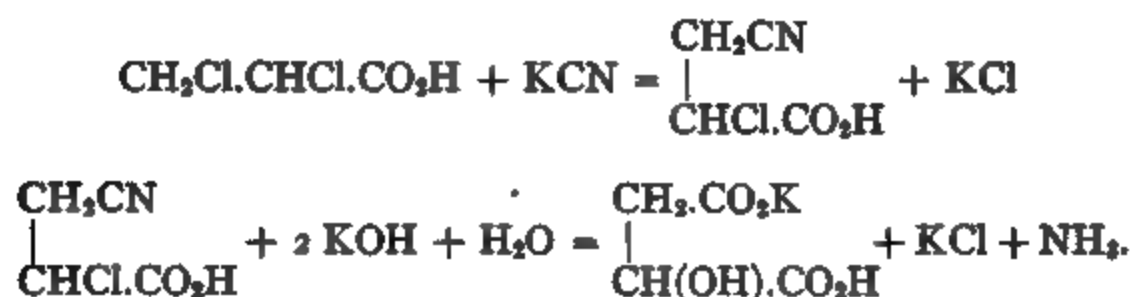
When oxidized *all* the malic acids give oxaloacetic acid  $\text{HOOC.OC.H}_2\text{CCOOH}$ , a proof of the presence of the secondary alcohol group.

The reactions just described show clearly that malic acid is monohydroxysuccinic acid. Nevertheless, if hydroxysuccinic acid is made by treating bromosuccinic acid with silver oxide and water, the product is not identical with ordinary malic acid, though the two resemble each other very closely. The acid thus obtained is

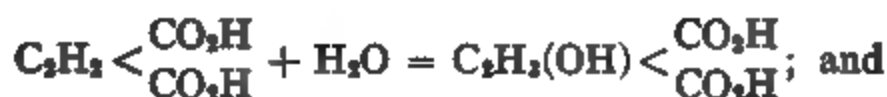
Inactive malic acid,  $C_2H_2(OH) < \begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$  — Inactive malic acid can be made not only by this method, but by several others, which show that the relation between it and succinic acid is that expressed in the formula given. Like ordinary malic acid, it is unquestionably a monohydroxysuccinic acid.

Other reactions for the preparation of inactive malic acid are:—

(1) By heating dichloropropionic acid (made from acrylic acid (286) and chlorine) with potassium cyanide and boiling the product with a solution of caustic potash:—



(2) By heating maleic or fumaric acid with water in a sealed tube:—



(3) By reducing racemic acid (200) with hydriodic acid.

By mixing equal quantities of the acid ammonium salts of the *d*-malic acid and the *l*-malic acid, dissolved in water, the acid ammonium salt of the inactive malic acid crystallizes out of the solution.

The properties of inactive malic acid are very much like those of the active malic acids. As regards their chemical conduct they are identical. The principal difference between



them is observed in their conduct towards polarized light. They present another case of *stereoisomerism* of the same kind as that referred to in connection with the stereoisomeric amyl alcohols (137) and the lactic acids (182).

**Dextromalic acid.**—Inactive malic acid bears the same relation to two active acids that inactive lactic acid bears to the two active varieties of that acid. When the cinchonine salt of inactive malic acid is subjected to fractional crystallization, it gives cinchonine *l*-malate and cinchonine *d*-malate.

One of these is a salt of *l*-malic acid, while the other is a salt of the stereoisomeric *d*-malic acid. The latter is also obtained by reducing *d*-tartaric acid (198) with hydriodic acid.

#### HYDROXY ACIDS, $C_nH_{2n-2}O_5$

These are *dihydroxy dibasic acids*. The chief members of the group are mesoxalic acid and the different modifications of tartaric acid.

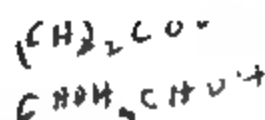
**Mesoxalic acid**,  $C_2H_2O_5$ ,  $C(OH)_2 < \begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$ .—This acid is obtained from alloxan, a derivative of uric acid (267). It has been made also by boiling dibromomalononic acid with baryta water and by oxidizing glycerol (169).

NOTE FOR STUDENT. — Explain these reactions.

The acid forms deliquescent needles. When its aqueous solution is boiled, it loses carbon dioxide and water, and glyoxylic acid, a half aldehyde of oxalic acid, is formed:—



When reduced, it gives tartronic acid. Mesoxalic acid affords an example of a rare condition; *viz.*, the existence of a compound in which two hydroxyls are in combination with the same carbon atom. This same condition exists in chloral hydrate (54). The acid readily loses water and passes over into the

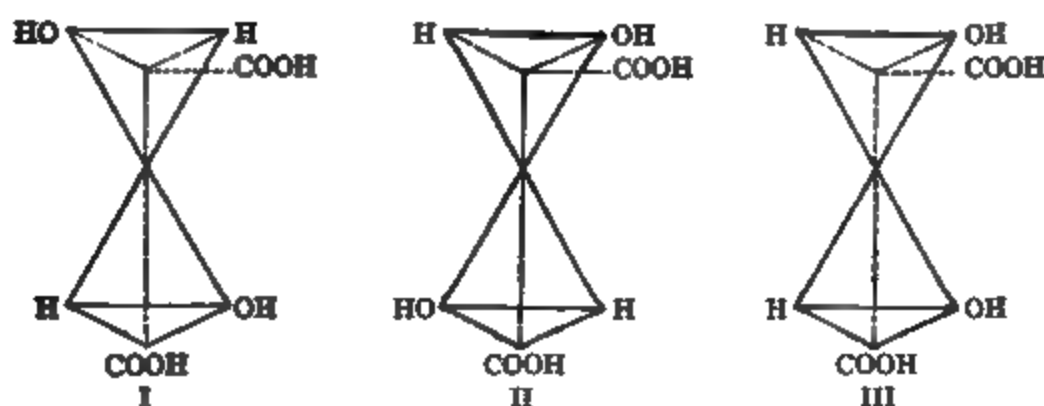


form  $OC(COOH)_2$ . With hydroxylamine it gives an oxime,  $HON=C(COOH)_2$ , and with phenylhydrazine a phenylhydrazone, thus showing the presence of the ketone group.

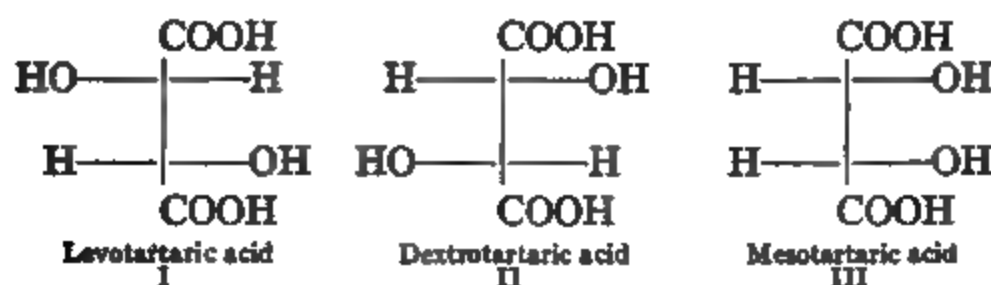
**Dihydroxysuccinic acids,  $HOOC.CHOH.CHOH.COOH$ .** — There are four acids known, all of which have this structural formula and which are stereoisomers. They are: —

- (1) Dextro- or *d*-tartaric acid, (m. p.  $170^\circ$ );
- (2) Levo- or *l*-tartaric acid, (m. p.  $170^\circ$ );
- (3) Racemic acid, (m. p.  $204^\circ$ ), which is made up of equal parts of the *d*- and the *l*-tartaric acids, and which is hence optically inactive; and
- (4) Mesotartaric acid, (m. p.  $140^\circ$ ), which is also optically inactive.

An examination of the above formula will show that it contains two asymmetric carbon atoms and that each of these asymmetric carbon atoms is united to the same groups, (H), (OH), (COOH), and (CHOH.COOH). There are then *three* possible arrangements in space of the groups connected with these two asymmetric carbon atoms: —

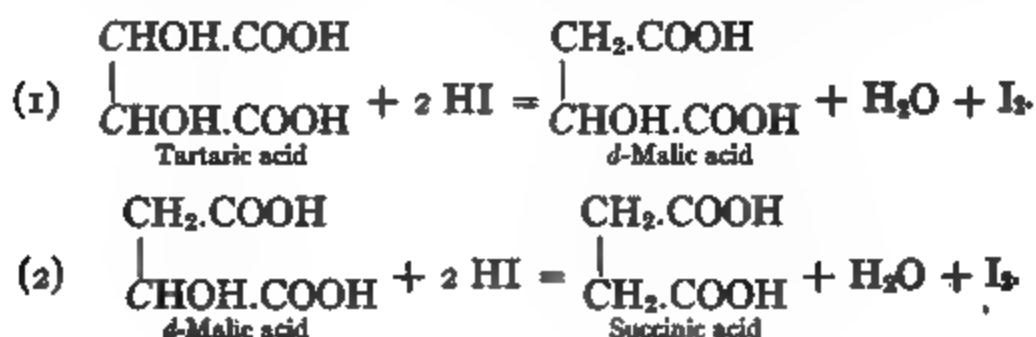


It is customary to project these *space* formulas on the plane of the paper and to omit the asymmetric carbon atoms, thus: —



I and II contain no plane of symmetry and bear the image-object relation to each other. They therefore represent the two optically active tartaric acids, and the combination of the two represents the inactive racemic acid. III has one plane of symmetry, as the upper half and the lower half of the molecule bear the image-object relation to each other. This form of tartaric acid should be optically *inactive*, for if the upper half of the molecule rotates the plane of polarized light to the right, the lower half will rotate it the *same* number of degrees to the left. This represents mesotartaric acid.

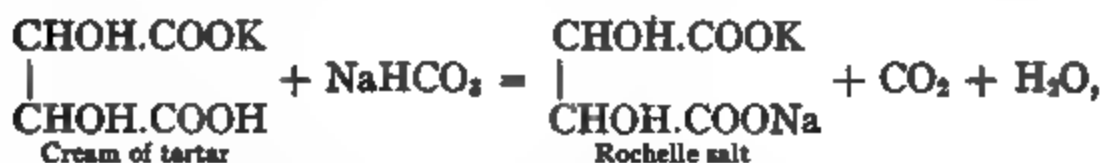
*d*-Tartaric acid. — This acid occurs very widely distributed in the vegetable kingdom, especially in fruits, sometimes in the free state, but generally in the form of the acid potassium salt, as in grapes. It also occurs in the berries of the mountain ash, in sumach berries, in tamarinds, mulberries, pineapples, etc., and in potatoes and cucumbers. It is prepared from argol or crude "tartar," which is an impure acid potassium tartrate. When the juice of the grape is fermented in making wine, this salt, which is insoluble in alcohol, is deposited together with the yeast, coloring matter, etc. It is heated with excess of hydrochloric acid, the solution filtered and boiled with milk of lime. The insoluble calcium salt is heated with water to remove soluble salts and decomposed with sulphuric or oxalic acid, and the tartaric acid purified by crystallization from water. The acid crystallizes from water in transparent, monoclinic prisms. It is readily soluble in water and alcohol, but is insoluble in ether. It melts at  $170^{\circ}$ . *Its solution turns the plane of polarized light to the right.* It is used in medicine, in dyeing, and in the manufacture of cream of tartar baking powders. Treated with hydriodic acid, it gives first *d*-malic acid, and then succinic acid: —



From these reactions it will be seen that tartaric acid is dihydroxysuccinic acid, and malic acid is monohydroxysuccinic acid.

Tartaric acid forms two series of salts. The neutral alkali salts are readily soluble, the neutral salts of the other metals are difficultly soluble or insoluble in water.

*Acid potassium tartrate*,  $\text{KOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$ , is difficultly soluble in water and is used as a test for tartaric acid. It is the chief constituent of argol or crude "tartar." In the pure form, as used in medicine and in baking powders, it is known as "cream of tartar." Cream of tartar baking powders are mixtures of cream of tartar and sodium bicarbonate with some starch or flour. With water, in the dough, the following reaction takes place:—

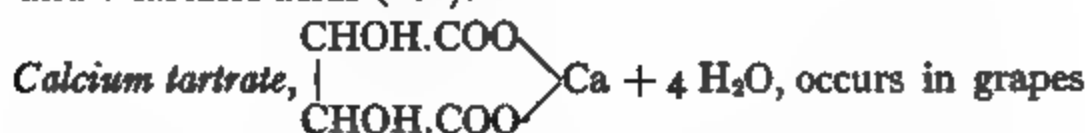


and the carbon dioxide liberated raises the dough.

*Sodium potassium tartrate*,  $\text{KOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COONa}$ , +  $4 \text{H}_2\text{O}$ . — This salt is characterized by its remarkable power of crystallization. It is known as *Rochelle salt* or *Seignette salt* and is much used as a laxative.

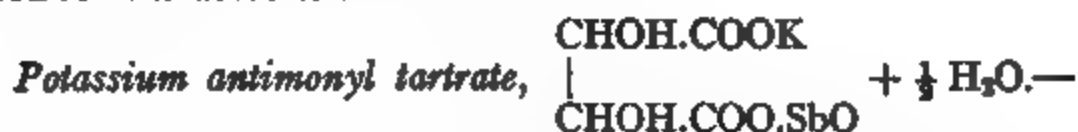
*Seidlitz powders* consist of (1) a mixture of Rochelle salt and sodium bicarbonate in the blue paper and (2) tartaric acid in the white paper. These are dissolved in water separately and the solutions brought together, when a rapid evolution of carbon dioxide takes place, making the dose less unpleasant to take. Isomorphous with Rochelle salt is

*Sodium ammonium tartrate*,  $\text{NaOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COONH}_4$  +  $4 \text{H}_2\text{O}$ , obtained in the separation of racemic acid into the *d*- and *l*-tartaric acids (201).



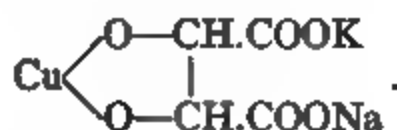
and in senna leaves. It is almost insoluble in water and is precipitated in crystalline form when a solution of calcium chlo-

ride is added to that of a neutral tartrate. This reaction is used for the detection of tartaric acid.



This salt is known as *tartar emetic*. It is prepared by dissolving four parts of antimony oxide and five parts of cream of tartar in 50 parts of water and allowing the solution to stand. It crystallizes in rhombic octahedra. It loses its water of crystallization partly in the air and is anhydrous at  $100^\circ$ . When the anhydrous salt is heated to  $160^\circ$ – $165^\circ$ , it loses a molecule of water and is converted into potassium antimony tartrate,  $\text{KSbC}_4\text{H}_2\text{O}_6$ , which gives tartar emetic when dissolved in water. Tartar emetic is extensively used as a mordant in dyeing and in medicine.

In the presence of Rochelle salt, sodium hydroxide does not precipitate copper hydroxide from a solution of copper sulphate. This is due to the formation of a complex soluble salt in which the copper replaces the two hydrogen atoms of the two hydroxyl groups: —



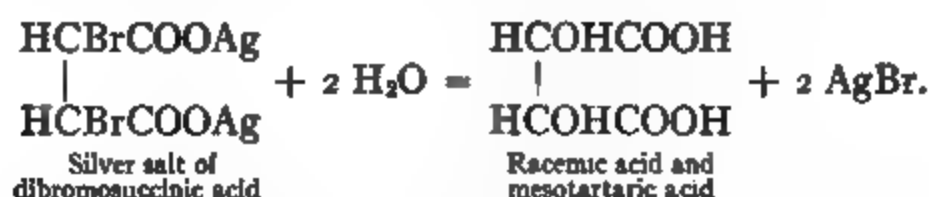
It is probable that a similar salt is present in Fehling's solution (223).

**Racemic acid,  $d\text{-C}_4\text{H}_6\text{O}_6 + l\text{-C}_4\text{H}_6\text{O}_6 + 2\text{H}_2\text{O}$ .** — This acid occurs together with *d*-tartaric acid in grapes and is obtained in the purification of the crude tartar by recrystallization. The acid potassium racemate being more soluble than the acid potassium tartrate remains in the mother liquors. *d*-Tartaric acid when heated with water in a sealed tube to  $160^\circ$ – $165^\circ$  is converted into racemic acid and mesotartaric acid. By heating 100 grams of *d*-tartaric acid with 700 grams of water containing 350 grams of sodium hydroxide for two hours, 50 grams of racemic acid and 30 grams of mesotartaric acid are obtained. When equal quantities of *d*-tartaric and *l*-tartaric acids, in concentrated aqueous solutions, are brought together, elevation of the tem-

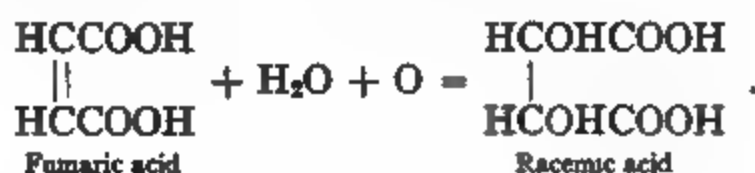
perature takes place, and racemic acid crystallizes out of the solution.

Racemic acid differs from the *d*- and the *l*-tartaric acids in being optically inactive. It crystallizes in triclinic prisms which contain 2 molecules of water of crystallization, whereas, the two active acids crystallize in monoclinic prisms without water of crystallization. Racemic acid loses its water of crystallization at  $110^{\circ}$  and then melts at  $204^{\circ}$ , with decomposition. In water, it is much less soluble than tartaric acid. Calcium racemate,  $2\text{CaC}_4\text{H}_4\text{O}_6 + 8\text{H}_2\text{O}$ , is much less soluble in water than calcium tartrate, and hence a solution of racemic acid gives a precipitate with a solution of calcium sulphate, while a solution of tartaric acid does not.

*Racemic acid is formed together with mesotartaric acid when the silver salt of dibromosuccinic acid is boiled with water:—*



Racemic acid is also formed when fumaric acid (294) is oxidized with a dilute solution of potassium permanganate:—



There are three methods by which racemic acid can be separated into the optically active tartaric acids, all of which we owe to Pasteur.

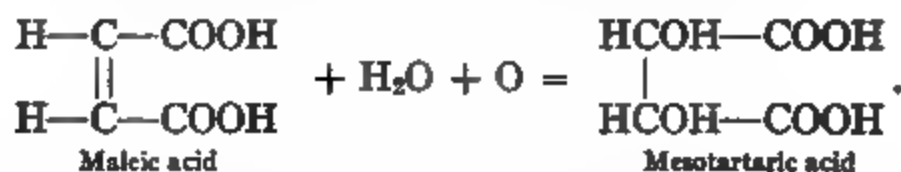
1. When sodium ammonium racemate is allowed to crystallize out of its solution, below  $27^{\circ}$ , it splits up into sodium ammonium *d*-tartrate and sodium ammonium *l*-tartrate. Since these two salts crystallize in forms on which right-handed and left-handed hemihedral faces are present, so that the two crystals bear the image-object relation, it is possible to separate them from each other mechanically. The acids obtained from the two sets of crystals are *d*-tartaric and *l*-tartaric acids.

2. The second method consists in combining racemic acid with an *optically active base*, e.g. *l*-cinchonine. Two salts are formed (1) *d*-acid-*l*-base and (2) *l*-acid-*l*-base. As these two salts do not bear the image-object relation to each other, they have different solubilities and can be separated by fractional crystallization.

3. The third method depends on the action of microorganisms. For example, *penicillium glaucum*, when grown in a solution of ammonium racemate, uses up the *d*-tartaric acid more rapidly than the *l*-tartaric acid, so that the solution becomes levorotatory.

Levotartaric acid,  $\text{HOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$ , has been obtained from racemic acid by the methods given above. It has the same melting point, the same solubilities, and in general the same physical and chemical properties as the dextroacid. It turns the plane of polarized light the *same* number of degrees to the *left* that the dextroacid turns it to the *right*. It has also been made by the oxidation of *l*-erythritol (173) and *l*-threose (216).

Mesotartaric acid,  $\text{HOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH} + \text{H}_2\text{O}$ . — Like racemic acid this acid is *optically inactive*, but unlike racemic acid it cannot be separated into optically active components. It is said to be optically inactive by internal compensation, while racemic acid is optically inactive by external compensation. (See space formulas, 197.) It is obtained together with racemic acid by heating tartaric acid with water in a sealed tube to  $160^\circ$ – $165^\circ$  or with a solution of caustic soda. It results also by the oxidation of natural erythritol (which is the internally compensated form of erythritol) and of phenol. It is formed when maleic acid (294) is oxidized with a dilute solution of potassium permanganate: —



Mesotartaric acid crystallizes in rectangular plates, having the composition  $\text{C}_4\text{H}_6\text{O}_6 + \text{H}_2\text{O}$ , and it also resembles racemic acid

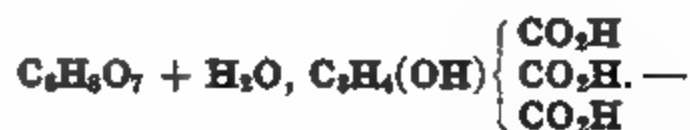
very closely in its chemical and physical properties. The dehydrated acid melts at  $140^{\circ}$ , and it differs also from the active tartaric acids and from racemic acid in solubility and other physical properties. It differs most markedly from its stereoisomers in that its acid potassium salt is readily soluble in water. It is not precipitated from its solution by a solution of calcium sulphate (distinction from racemic acid).

#### HYDROXY ACIDS, $C_nH_{2n-4}O_7$

These are *monohydroxytribasic acids*. Citric acid is the only one of importance.

Citric acid, hydroxytricarballic acid,

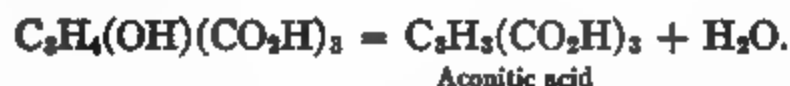
$C_3H_4O_7$



Citric acid, like malic and tartaric acids, is widely distributed in nature in many varieties of fruit, especially in lemons and in grapefruit, in which it occurs in the free condition. It is found in currants, whortleberries, raspberries, gooseberries, etc., and in milk.

It is prepared from lemon juice, and also by the fermentation of glucose by *citromyces pfefferianus* and a few other mould fungi. After boiling and filtering the solution it is boiled with milk of lime. The calcium salt thus obtained in the form of a precipitate is collected, and decomposed with the calculated quantity of sulphuric acid. One hundred parts of lemons yield  $5\frac{1}{2}$  parts of the acid.

Citric acid crystallizes with a molecule of water of crystallization in rhombic prisms which are very easily soluble in water and alcohol. The crystallized acid melts at about  $100^{\circ}$ , the anhydrous at  $153^{\circ}$ . Heated to  $175^{\circ}$ , it loses water and yields aconitic acid (295):—



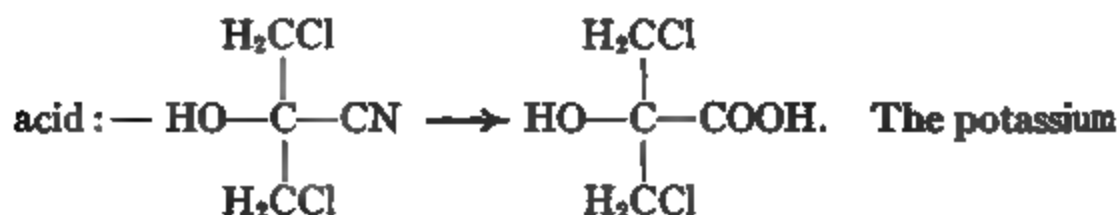
Aconitic acid takes up hydrogen, and is transformed into tricarballic acid (173). Thus a clear connection between



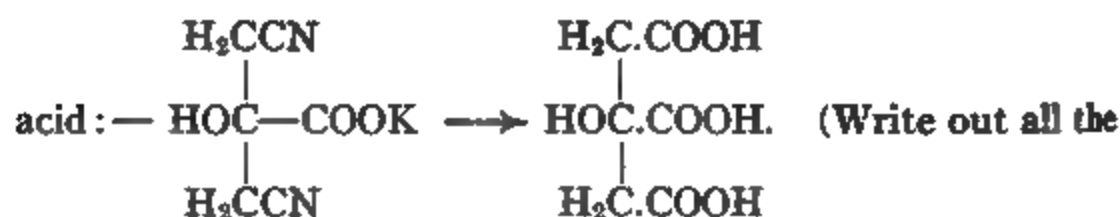
tricarballic acid and citric acid is traced; the latter is hydroxytricarballic acid. Citric acid can be made from dichlorohydrin by first converting this into dichloroacetone by oxidation: —



The dichloroacetone is combined with hydrocyanic acid to form the cyanhydrin, and this is hydrolyzed to the corresponding



salt of this acid is then heated with a concentrated solution of potassium cyanide, and the product hydrolyzed to citric



equations.)

This synthesis shows that the hydroxyl in citric acid is in combination with the central carbon atom.

When rapidly heated to a temperature above  $175^\circ$ , citric acid first gives aconitic acid. This loses water and carbon dioxide and gives *itaconic anhydride* (295). This anhydride is then partly converted into *citraconic anhydride* (295) by the action of heat.

Citric acid is used in calico printing, in medicine, in the manufacture of lemonade and other drinks and as a corrective against scurvy. It is also used in analytical chemistry and, in the form of ferric ammonium citrate, in the manufacture of blue print paper.

*Citrates.* — A few of the salts of citric acid are: —

*Monopotassium citrate*,  $\text{KH}_2\text{C}_6\text{H}_5\text{O}_7 + 2 \text{H}_2\text{O}$ ;

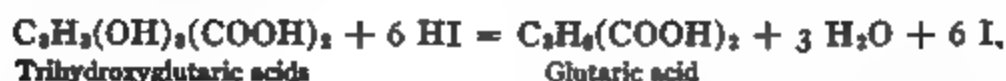
*Dipotassium citrate*,  $\text{K}_2\text{H.C}_6\text{H}_5\text{O}_7$ ;

*Tripotassium citrate*,  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$ . All these potassium salts are easily soluble in water.

*Calcium citrate*,  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 + 4 \text{H}_2\text{O}$ . — This salt is formed by boiling a solution of a citrate of an alkali metal and calcium chloride. It is more easily soluble in cold than in hot water; hence boiling causes a precipitate in dilute solutions.

*Magnesium citrate*,  $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2 + 14 \text{H}_2\text{O}$ . — This is made by dissolving magnesia in a solution of citric acid. It is used as a laxative.

**Trihydroxyglutaric acids**,  $\text{HOOC}(\text{CHOH})_2\text{COOH}$ . — These stereoisomeric acids are important as oxidation products of the pentoses,  $\text{CHO}(\text{CHOH})_2\text{CH}_2\text{OH}$ . They are also formed by the oxidation of the pentacid alcohols, adonitol, arabitol, and xylitol, and of the monobasic acids arabonic, ribonic, xylonic, and lyxonic acids (191). Ribotrihydroxyglutaric acid obtained by the oxidation of ribose and ribonic acid and xylotrihydroxyglutaric acid by the oxidation of xylose and xylonic acid are optically inactive by intramolecular compensation. *d*- and *l*-Trihydroxyglutaric acids and the racemic modification (*dl*-form) are also known. Thus all five of the acids predicted by the theory are known. All these stereoisomers are reduced to glutaric acid by heating with hydriodic acid: —



This proves the presence of the normal carbon chain in all these acids, and that the isomerism is due to the asymmetric carbon atoms.

**Tetrahydroxyadipic acids**,  $\text{HOOC}(\text{CHOH})_4\text{COOH}$ . — These stereoisomeric acids result from the oxidation of the hexoses,  $\text{CHO}(\text{CHOH})_4\text{CH}_2\text{OH}$ , or of the hexacid alcohols mannitol, dulcitol, and sorbitol. They are also formed by the oxidation of the hexonic acids,  $\text{HOOC}(\text{CHOH})_4\text{CH}_2\text{OH}$  (191). *Saccharic acid*, first obtained by the oxidation of cane sugar (saccharose) with nitric acid, is known in a dextro-, levo-, and racemic (*dl*-) form. It results from the oxidation of sorbitol, glucose, gulose, gluconic and gulonic acids. *Mannosaccharic*



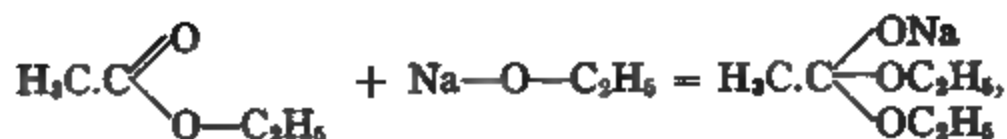
It combines with sodium bisulphite and with ammonia, and reduces an ammoniacal solution of silver nitrate. On reduction it gives glycolic acid, and on oxidation oxalic acid. (Write out all the equations.)

**Pyruvic or pyroracemic acid, propanone acid,  $\text{CH}_3\text{CO}\cdot\text{COOH}$ ,** is an example of an  $\alpha$ -ketone-acid. As its name indicates, it is obtained by distilling racemic (or tartaric) acid with potassium bisulphate. In this decomposition glyceric acid is first formed from the tartaric acid by the elimination of carbon dioxide, which gives pyruvic acid by the loss of water:—

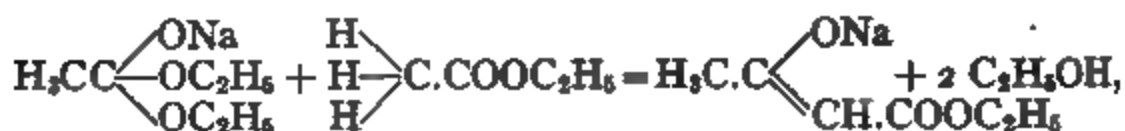


Pyruvic acid results from the oxidation of the lactic acids, and it can also be made from acetyl chloride, by converting this into acetyl cyanide and hydrolyzing. Its constitution follows from these methods of preparation. It is a liquid, solidifying, when pure, at  $13^\circ$ – $14^\circ$  and boiling at  $165^\circ$ – $170^\circ$  (with slight decomposition), and soluble in water, alcohol, and ether. It has the odor of acetic acid. Owing to the acidifying influence of the carbonyl group, it is a *strong* acid, much stronger than propionic acid. When reduced, it gives *dl*-lactic acid. Towards hydroxylamine, phenylhydrazine, and hydrocyanic acid it reacts as a ketone. (Write out the equations.) It is made technically and is used in the preparation of atophan and related compounds.

**Acetoacetic acid, butanone-3-acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOH}$ ,** is the best known  $\beta$ -ketone acid. It is obtained by very careful hydrolysis of its ethyl ester at a low temperature. It is extremely unstable, decomposing into carbon dioxide and acetone when set free from its salts. This instability sharply distinguishes the  $\beta$ -ketone acids from the  $\alpha$ - and  $\gamma$ -ketone acids which are stable. It is present in the urine of persons affected with *diabetes mellitus*. The ethyl ester is prepared by the action of sodium on ethyl acetate containing a small amount of ethyl alcohol. The sodium first acts on the ethyl alcohol, forming sodium ethylate. This then reacts with the ethyl acetate, forming a salt of orthoacetic acid:—



which at once reacts with another molecule of ethyl acetate:—



regenerating the alcohol, and forming the sodium salt of the ester. The ester is obtained by treating this sodium salt with acetic acid, the product first formed passing over into the more stable ketone form:—



**Ethyl acetoacetate** is a colorless liquid boiling at  $181^\circ$ , having a pleasant fruity odor. It is only slightly soluble in water, but readily soluble in alcohol and ether. It is volatile with steam.

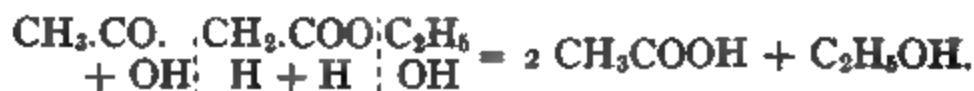
It undergoes hydrolysis in three ways:—

1. *Normal hydrolysis*, giving the acid and alcohol. (See above.)

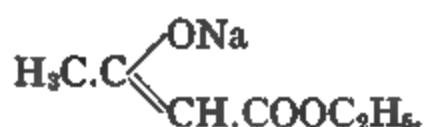
2. *Ketone hydrolysis*, brought about by heating the ester with dilute sulphuric acid or with dilute aqueous alkali:—



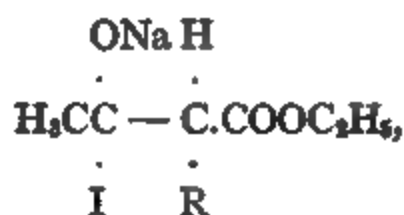
3. *Acid hydrolysis*, which takes place with concentrated alcoholic potash or soda:—



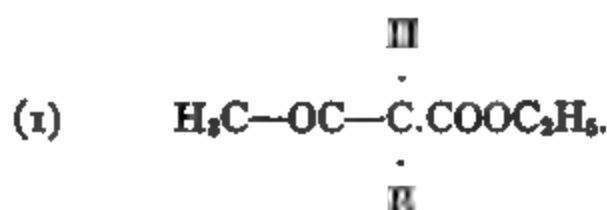
When treated with sodium or sodium ethylate, the ester gives the sodium salt:—



This forms an addition product with an alkyl iodide: —



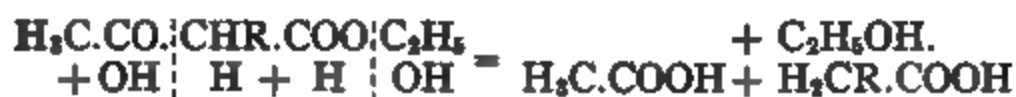
which by the elimination of sodium iodide gives an alkyl derivative of acetoacetic ester: —



This compound undergoes the ketone hydrolysis and the acid hydrolysis in the same way that ethyl acetoacetate does, yielding homologues of acetone:—



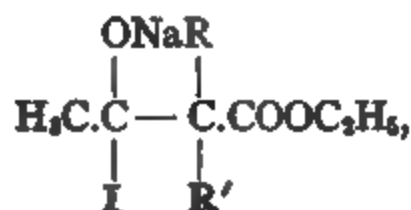
and homologues of acetic acid: —



The compound (I) also reacts with sodium or sodium ethylate to give a sodium salt: —



and with an alkyl iodide this forms an addition product: —



which by the elimination of sodium iodide gives a dialkyl derivative of acetoacetic ester:—



This compound also undergoes the ketone hydrolysis:—



giving higher homologues of acetone; and the acid hydrolysis:—



giving higher homologues of acetic acid.

This *acetoacetic ester synthesis*, as it is called, has been of great value in building up the homologues of acetone and acetic acid and in the synthesis of numerous other compounds. Ethyl acetoacetate is one of the most valuable synthetic reagents of organic chemistry. It is made on the large scale and is used in the manufacture of antipyrine, salipyrine, pyramidon, and perfumes (ionone). It is also used in the preparation of dimethylglyoxime and of dyes (dianil yellow).

Ethyl acetoacetate has been isolated in two forms. By cooling to a low temperature, the ketone form,  $\text{CH}_3\text{CO.CH}_2\text{COOC}_2\text{H}_5$ , separates in crystals melting at  $-39^\circ$ . The enol form,  $\text{H}_3\text{C.C(OH)=CH.COOC}_2\text{H}_5$ , is obtained from the sodium compound suspended in petroleum ether by treating it, at a very low temperature, with an equivalent quantity of anhydrous hydrochloric acid, filtering off the sodium chloride formed and evaporating the petroleum ether at a low temperature. This form of the ester does not solidify until cooled in liquid air. The two forms differ in solubility and also in their chemical reactions and physical properties. The enol form reacts with a solution of ferric chloride, giving a violet coloration, while the ketone form gives no color. The enol form dissolves at once in caustic alkalies, forming a salt, while the ketone form does not (except as it is slowly transformed into the enol form). With bromine the enol form combines instantaneously, while the

ketone form does not, and this difference is made use of to determine the amount of the enol form present in the ester. In the liquid state the ester contains about 90 per cent of the ketone form, the two forms being in equilibrium. Ethyl acetoacetate is a typical tautomeric compound (96) and may react either in the ketone or the enol form. The sodium salt is a derivative of the enol form as shown above.

The reactions of ethyl acetoacetate are in accord with the view that it is a tautomeric substance. For example, it reacts with sodium bisulphite, with hydrocyanic acid, and with hydroxylamine just as the ketones do. (Write out the equations.) With ammonia, however, it gives  $\beta$ -aminocrotonic acid,  $\text{CH}_3\text{C}(\text{NH}_2)=\text{CHCOOH}$ , and, when treated with phosphorus pentachloride,  $\beta$ -chlorocrotonic acid,  $\text{CH}_3\text{CCl}=\text{CHCOOH}$ . These reactions are best explained by assuming the enol formula for ethyl acetoacetate,  $\text{CH}_3\text{C}(\text{OH})=\text{CHCOOC}_2\text{H}_5$  (ethyl  $\beta$ -hydroxycrotonate).

Levulic acid, pentanone-4 acid,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is a  $\gamma$ -ketone acid. When hexoses (especially levulose) are boiled with concentrated hydrochloric acid, this acid, together with formic acid and humus substances, is formed, and this is the best method of preparation. Its formation from the hexoses is characteristic and is used to determine the presence of these sugars. Levulic acid is a crystalline substance melting at  $37.2^\circ$ , soluble in water, and so stable that it can be distilled (under reduced pressure). It boils, with only slight decomposition, at about  $250^\circ$ . It reacts with hydroxylamine to form an oxime, with phenylhydrazine to give a phenylhydrazone, and forms an addition product with hydrocyanic acid, showing the presence of the ketone group. On reduction with sodium amalgam it gives the sodium salt of  $\gamma$ -hydroxyvaleric acid:—





## CHAPTER XI

### CARBOHYDRATES

AMONG the mixed compounds are the important substances known as *carbohydrates*. This name was originally given to them because they consist of carbon in combination with hydrogen and oxygen in the proportion to form water, as shown in the formulas, for glucose,  $C_6H_{12}O_6$ , starch,  $C_6H_{10}O_5$ , etc. The name is, however, inaccurate, as some substances belonging to this group are now known that do not contain hydrogen and oxygen in the proportion to form water. Such a substance, for example, is rhamnose,  $C_6H_{12}O_5$ . Further, there are many carbon compounds, as, for example, formic aldehyde,  $CH_2O$ , acetic acid,  $C_2H_4O_2$ , and lactic acid,  $C_3H_6O_3$ , that contain hydrogen and oxygen in the proportion characteristic of most of the carbohydrates, but do not belong to this group. The name carbohydrate has, however, been used so long that it would be difficult to supplant it.

The carbohydrates may be conveniently classified under three heads. These are:—

1. *Monosaccharoses, monoses, or simple sugars*. — Examples of these are glucose, fructose, arabinose, and mannose.
2. *Polysaccharoses, polyoses, or complex sugars*. — Examples are cane sugar, sugar of milk, maltose, isomaltose, and raffinose.
3. *Colloidal polysaccharoses or polyoses*. — Examples are cellulose, starch, and glycogen.

The polysaccharoses give the simple sugars on hydrolysis with dilute acids.

The monoses are the simplest carbohydrates. Those which are best known have the composition  $C_6H_{12}O_6$ , and are related to the hexacid alcohols, sorbitol, mannitol, and dulcitol,  $C_6H_8(OH)_6$ . There are, however, simpler ones, such as arabinose,  $C_5H_{10}O_5$ , erythrose,  $C_4H_8O_4$ , and glycerose,  $C_3H_6O_3$ ;

and some that are more complex, as heptose,  $C_7H_{14}O_7$ , octose,  $C_8H_{16}O_8$ , and nonose,  $C_9H_{18}O_9$ . The monoses, therefore, fall into classes which are called *trioses*, *tetroses*, *pentoses*, *hexoses*, etc., according to the number of *oxygen atoms* contained in them.

By methods that will be explained below, it has been shown that the monoses or simple sugars are *aldehyde alcohols* (*aldoses*)

or *ketone alcohols* (*ketoses*) containing the group,  $\begin{array}{c} \text{---CHOH} \\ | \\ \text{---CO} \end{array}$ .

The termination *-ose* is reserved for the sugars.

## I. MONOSACCHAROSES, MONOSES

### A. Trioses, $C_3H_6O_3$

The simplest *aldotriose* is glyceric aldehyde,



the simplest *ketotriose* is dihydroxyacetone,

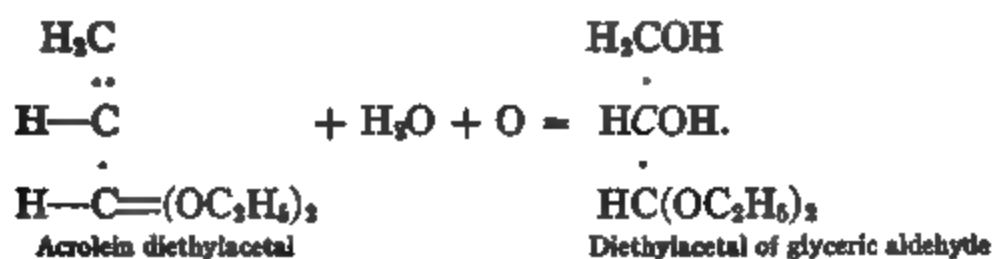


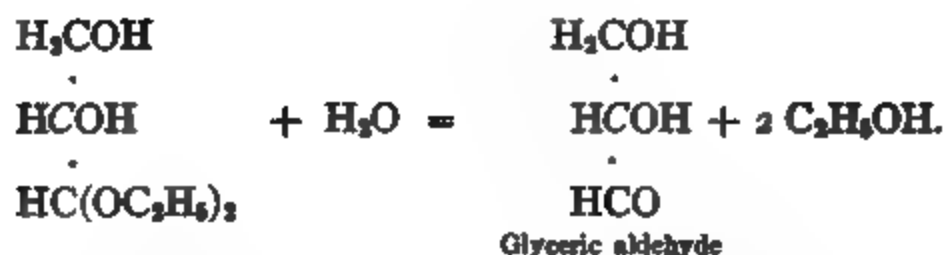
When glycerol is oxidized with bromine water in the presence of soda or with hydrogen peroxide, a mixture of these two substances, known as *glycerose*, is obtained. When this mixture is treated with dilute alkalis, it gives  $\alpha$ -acrose (*dl*-fructose),  $C_6H_{12}O_6$  (232).

*dl*-Glyceric aldehyde, propane-diol-2, 3-al,

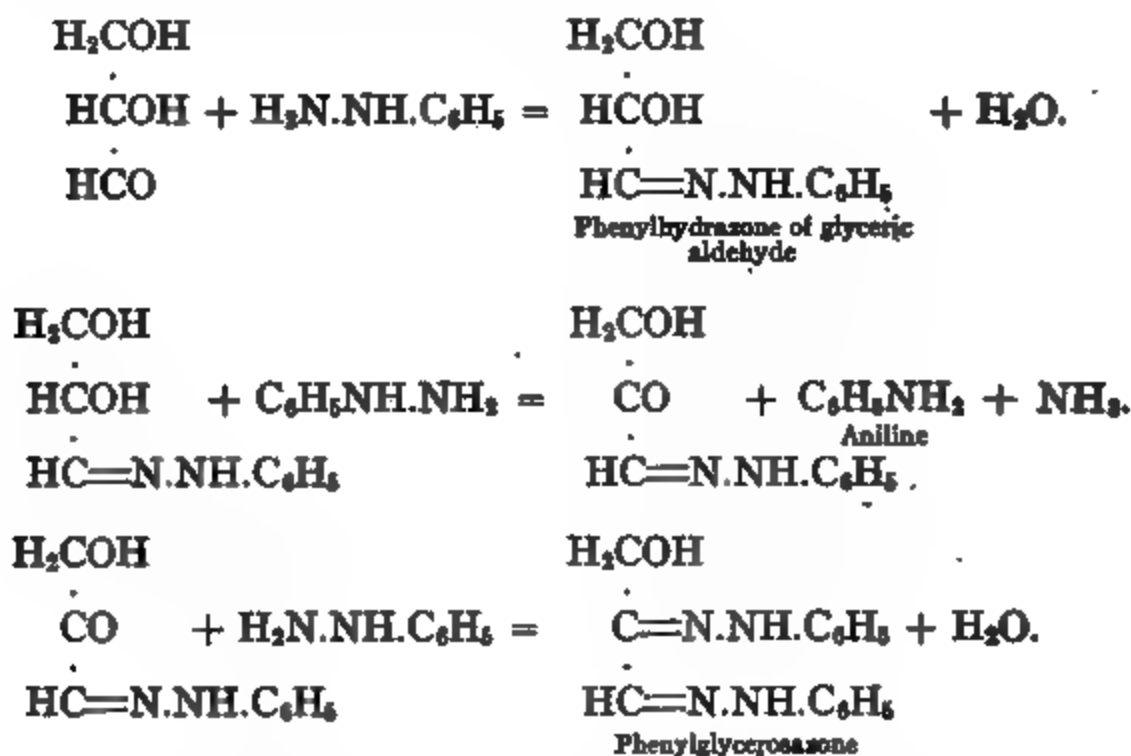


is made by oxidizing acrolein diethylacetal with a dilute solution of potassium permanganate and hydrolyzing the acetal formed:—





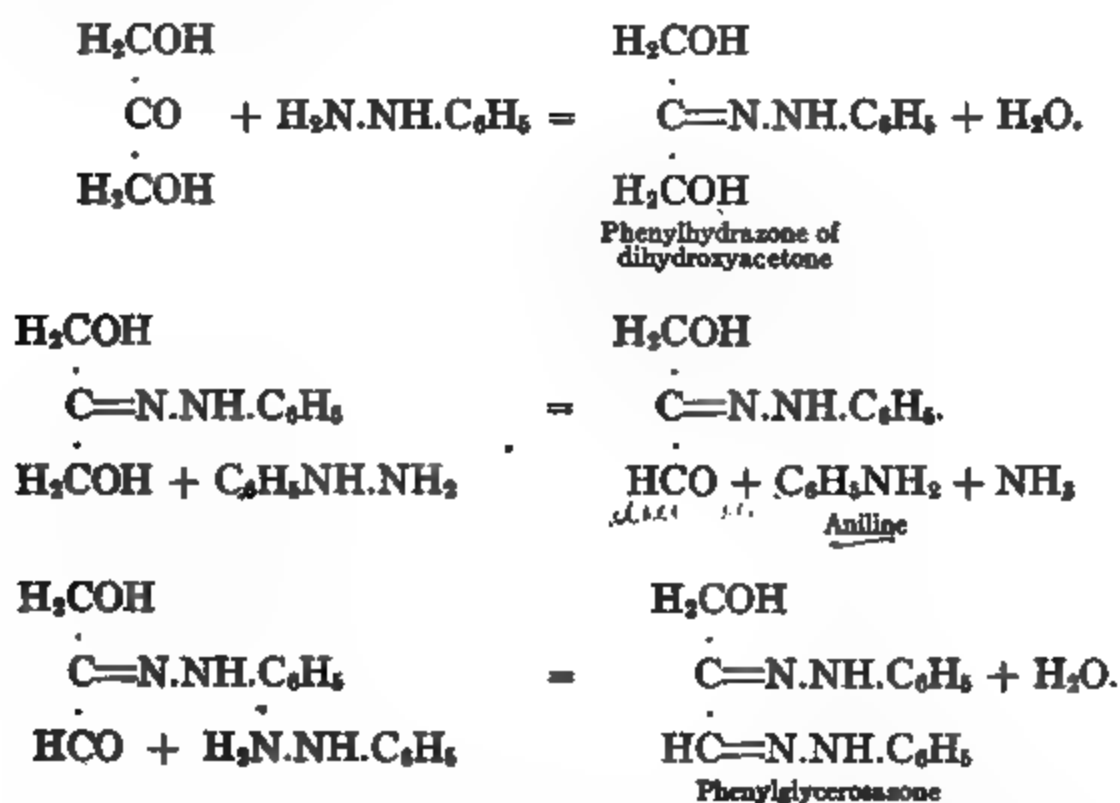
It crystallizes in needles, tastes sweet, is soluble in water, but only slightly soluble in organic solvents, is not hygroscopic, and not volatile with steam. It melts at  $138^\circ$  and reduces Fehling's solution in the cold. Bromine water oxidizes it to *dl*-glyceric acid. With phenylhydrazine in solution in acetic acid it gives the same phenylglycerosazone (m. p.  $131^\circ$ – $132^\circ$ ) that dihydroxyacetone does:—



The glyceric aldehyde first reacts with phenylhydrazine to form the phenylhydrazone, just as any aldehyde does. (See Phenylhydrazine.) With an excess of phenylhydrazine the secondary alcohol group is changed to a *ketone* group by the loss of two hydrogen atoms. This reduces a molecule of phenylhydrazine to aniline and ammonia. The compound containing the *ketone* group then reacts with another molecule of phenylhydrazine to give the phenylglycerosazone as shown above.

Glyceric aldehyde is slowly converted into alcohol and carbon dioxide by yeast or a solution of zymase. The crystallized glyceric aldehyde is bimolecular. In aqueous solution it slowly changes to the monomolecular form, more quickly when heated. Glyceric aldehyde is optically inactive, as it is a mixture of the *d*- and the *l*-forms. (Does it contain an asymmetric carbon atom?)

Dihydroxyacetone, propane-diol-1, 3-one,  $\text{CH}_2\text{OH}.\text{CO}.\text{CH}_2\text{OH}$ , is made by oxidizing glycerol by means of the sorbose bacteria. When its aqueous solution is evaporated in a vacuum, colorless prisms are obtained, which melt at about  $80^\circ$ . This form is bimolecular; in aqueous solution it changes to the monomolecular form. It reduces Fehling's solution in the cold and gives the same phenylglycerosazone with phenylhydrazine that glyceric aldehyde does:—

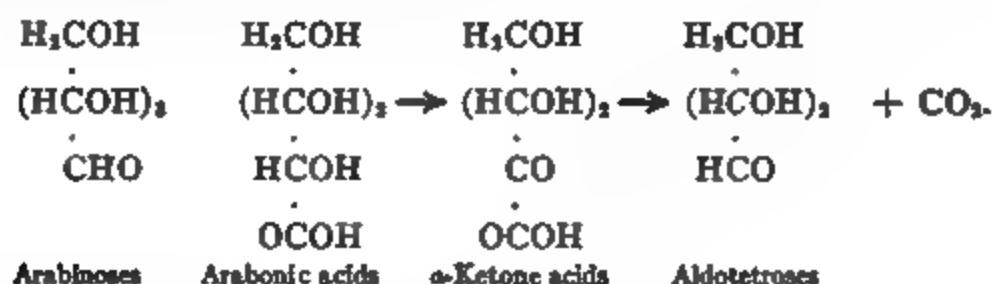


In these reactions the dihydroxyacetone first forms the phenylhydrazone, just as any ketone does; and with excess of phenylhydrazine this loses two hydrogen atoms from one of the primary alcohol groups, converting it into an *aldehyde* group, which at once reacts with another molecule of phenylhydrazine to give

phenylglycerosazone, as shown above. Dihydroxyacetone has a sweet taste and ferments with yeast or zymase. It forms a well-crystallized compound with sodium bisulphite and an oxime (m. p.  $83^{\circ}$ – $84^{\circ}$ ) with hydroxylamine. Both dihydroxyacetone and glyceric aldehyde give glycerol on reduction.

### B. Tetroses, $C_4H_8O_4$

Four stereoisomeric *aldotetroses*,  $CH_2OH.CHOH.CHOH.CHO$ , butane-triol-2, 3, 4-als, are theoretically possible as the formula contains two asymmetric carbon atoms, and the groups attached to the two asymmetric carbon atoms are not the same. *d*- and *l*-Erythrose and the inactive (*dl*-) form of erythrose have been obtained by the degradation of the *d*-, *l*-, and *dl*-arabonic acids by oxidizing them with hydrogen peroxide in the presence of ferric salts:—



*l*-Threose has been obtained in a similar manner from *l*-xylonic acid. The formula for the simplest ketotetrose,



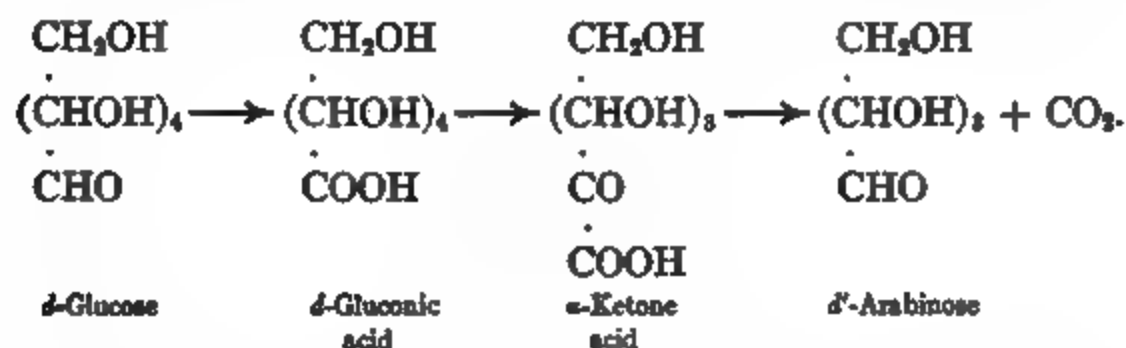
butane-triol-1, 3, 4-one-2, contains only one asymmetric carbon atom, and therefore only *d*-, *l*-, and *dl*-forms are to be expected. *d*-Erythrulose results from the oxidation of erythritol by the sorbose bacteria. It is not attacked by bromine water, while the erythroses and threose are oxidized by this reagent to erythronic and threonic acids. Further oxidation of these acids gives the tartaric acids. *dl*-Erythrulose results from the oxidation of the natural erythritol with hydrogen peroxide in the presence of iron salts or with bromine. All the tetroses are known only in the form of syrups, and they do not undergo fermentation with yeast.

### C. Pentoses, $C_5H_{10}O_5$

Eight optically active stereoisomeric aldopentoses,  $CH_2OH.(CHOH)_3CHO$ , pentane-tetrol-2, 3, 4, 5-als, are theoretically possible, and all are known with the exception of *l*-lyxose. None of the pentoses occur *free* in nature.

***l'*-Arabinose**,<sup>1</sup> in the form of polysaccharoses known as "arabans,"<sup>2</sup> is very widely distributed in the plant world. It was first obtained by the hydrolysis of gum arabic, and hence its name. It can also be made by the hydrolysis, with mineral acids, of cherry gum or of sugar beet chips, after extracting the beet sugar. It crystallizes in prisms, melts about 160°, is very soluble in water, and has a sweet taste. Although this variety of arabinose is dextrorotatory it is called *l'*-arabinose, because of its close relationship in configuration to *l*-glucose and *l*-mannose.

***d'*-Arabinose** was first made artificially by the degradation of *d*-glucose (220) by oxidizing *d*-gluconic acid with hydrogen peroxide in the presence of ferric salts:—



It has also been obtained by the hydrolysis of the glucosides, barbaloin and isobarbaloin, contained in Barbados aloes.

***dl*-Arabinose** was first obtained by combining the *d*- and *l*-varieties. In the disease known as pentosuria this sugar is present in the urine. On reduction, the arabinoses give the arabitols, and on oxidation, first, the arabonic acids and then the trihydroxyglutaric acids (205).

**Xyloses.**—*l'*-Xylose in the form of "xylans" is widely distributed in plants. It is best made from wood gum (xylan), and hence the name, or from corn cobs, by hydrolysis with mineral acids. It is sometimes called wood sugar. It tastes very sweet, is dextrorotatory, yields xylitol on reduction and

<sup>1</sup> The sign *l'* signifies that the substance is dextrorotatory, but is derived from, or closely related to, substances that are levorotatory. Similarly the sign *d'* signifies that the substance is levorotatory, but derived from, or related to, substances that are dextrorotatory.

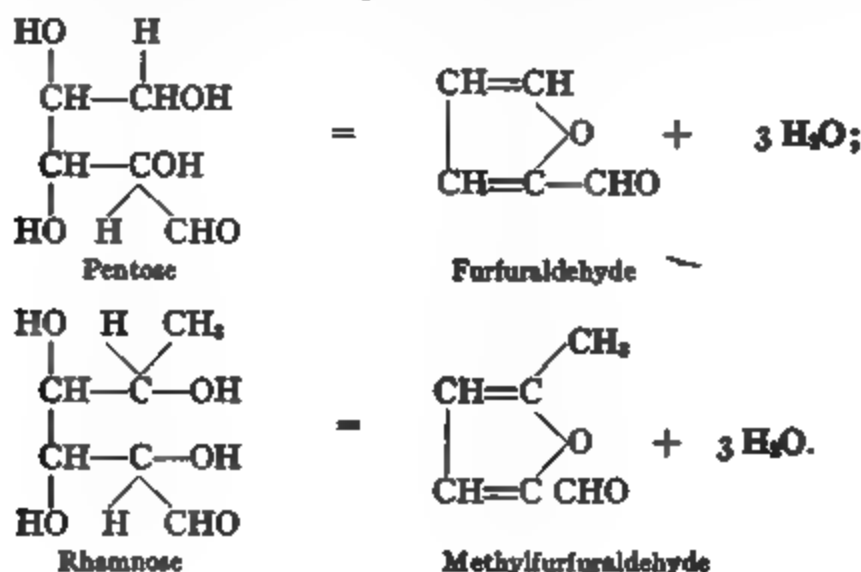
<sup>2</sup> These are starch-like carbohydrates which undergo hydrolysis to the corresponding sugars. Thus arabans give arabinose, xylans, xylose, etc.

*l'*-xylonic and xylotrihydroxyglutaric acids on oxidation. *d'*-Xylose has been made by the degradation of *d*-gulonic acid by oxidizing it with hydrogen peroxide in the presence of ferric salts. (See Arabinose.) The *dl*-variety results when a mixture of equal parts of the active components is crystallized from alcohol.

**Riboses.** — *l'*-Ribose is obtained from *l*-arabonic acid by heating it with pyridine, when it undergoes molecular rearrangement into *l'*-ribonic acid. On reducing the lactone of this acid *l'*-ribose is formed. It has a sweet taste, is dextrorotatory, and melts at 87°. On reduction it gives adonitol, and on oxidation *l'*-ribonic and ribotrihydroxyglutaric acids. *d'*-Ribose has been obtained from certain nucleic acids by hydrolysis. It is levorotatory and melts at 86°–87°.

**Lyxose.** — *d'*-Lyxose is made from *l*-xylonic acid, which undergoes molecular rearrangement on heating with pyridine into *d'*-lyxonic acid. When the lactone of this acid is reduced it gives *d'*-lyxose. It has also been made by the degradation of *d*-galactonic acid. (See *d'*-Arabinose.) The name is derived from xylose by reversing the order of the letters xyl-. It is levorotatory and gives *d'*-arabitol on reduction and *d'*-lyxonic and trihydroxyglutaric acids on oxidation.

**Rhamnose** occurs in the plant kingdom in a very large number of glucosides (quercitrin, xanthorhamnin, etc.), from which it is prepared by hydrolysis. It crystallizes well from water ( $C_6H_{12}O_5 + H_2O$ ), tastes sweet, melts at 93°–94°, and is optically active. On reduction it gives rhamnitol, and on oxidation with bromine water rhamnonic acid. It is a methyl-pentose,  $CH_3(CHOH)_4CHO$ , since it gives methylfurfuraldehyde on distillation with hydrochloric acid, whereas the above mentioned pentoses give furfuraldehyde. This reaction is characteristic of the pentoses and pentosans, and is used for their quantitative determination:—



Isorhamnose, rhodose, isorhodose, fucose, and quinovose are stereoisomers of rhamnose. None of the pentoses are fermentable with yeast.

Ketopentoses have not yet been isolated in the pure condition.

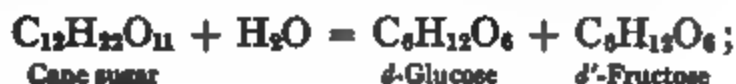
#### D. Hexoses, $C_6H_{12}O_6$

The hexoses are the most important monoses and the ones which have been longest known. Three aldohexoses,  $CH_2OH.(CHOH)_4.CHO$ , *d*-glucose, *d*-mannose, and *d*-galactose, and one ketohexose,  $CH_2OH.(CHOH)_3.CO.CH_2OH$ , *d'*-fructose, occur in nature.

Sixteen optically active, stereoisomeric, aldohexoses,  $CH_2OH(CHOH)_4CHO$ , hexane-pentol-2, 3, 4, 5, 6-als, are theoretically possible, of which thirteen are now known.

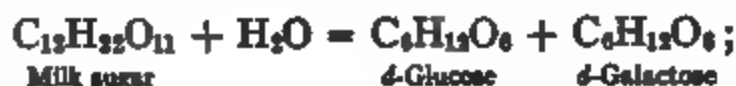
*d*-Glucose is the most important monose. On account of its abundant occurrence in grapes it is ordinarily called grape sugar. As its solution is dextrorotatory, it was formerly called *dextrose* to distinguish it from the levorotatory fructose (*levulose*). As *d*-, *l*-, and *dl*-forms of glucose are now known, this name has been discarded. In the *free* condition *d*-glucose occurs widely distributed in the plant world, frequently together with *d'*-fructose, sometimes together with cane sugar, especially in sweet fruits.

A mixture of *d*-glucose and *d'*-fructose (invert sugar) forms the principal constituent of honey. *d*-Glucose occurs regularly in small quantity in blood, lymph, and in human urine (less than 0.1 per cent). In the disease *diabetes mellitus* the amount of *d*-glucose in the urine may rise to 12 per cent, corresponding to 500 to 1000 grams per day. *d*-Glucose also occurs in the free state in the white and yolk of the egg. In the combined state it occurs in many *glucosides* (527). These give glucose as one of the products on hydrolysis with dilute mineral acids or with certain enzymes. It is a constituent of the polyoses or complex sugars,  $C_{12}H_{22}O_{11}$ , from which it results on hydrolysis. Thus, cane sugar is hydrolyzed by dilute mineral acids or by the enzyme, invertase, to *d*-glucose and *d'*-fructose:—





milk sugar, or lactose, into *d*-glucose and *d*-galactose by acids or lactase : —



and malt sugar, or maltose, into two molecules of *d*-glucose by acids or maltase : —



In plants *d*-glucose is very abundant in the form of the polysaccharoses, starch and cellulose, while in animals it occurs as the polyose, glycogen. These are hydrolyzed by dilute mineral acids giving *d*-glucose as the final product :—



*d*-Glucose is best prepared in the laboratory by the hydrolysis of pure cane sugar with hydrochloric acid. It is separated from the *d'*-fructose, formed at the same time, by crystallization from alcohol. On the large scale *d*-glucose is made by the hydrolysis of starch with hydrochloric acid. In this country corn starch is used; in Europe potato starch.

The commercial name "glucose" must be distinguished from *d*-glucose used by the chemist for the chemical individual,  $\text{C}_6\text{H}_{12}\text{O}_6$ . The commercial glucose is a syrup, which it would be much better to call corn syrup. It is made by the partial hydrolysis of the starch of Indian corn with dilute hydrochloric acid, in closed vessels under a steam pressure of 35 lb. The hydrolysis of the starch is only carried to a point where there is about 12 per cent of reducing sugars present. When the conversion of the starch has reached this point the liquid is neutralized with a dilute solution of sodium carbonate, filtered, decolorized with bone-char, and evaporated in vacuum pans to a thick syrup. Enormous quantities of this commercial glucose are used in the manufacture of confectionery. It has the property of preventing the cane sugar, with which it is usually mixed, from crystallizing or

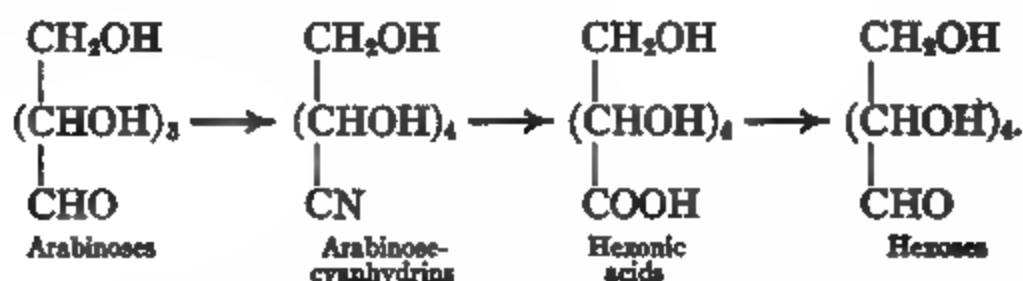
"graining." It is also used as a table syrup, either alone or mixed with cane sugar syrup (molasses), and in the manufacture of jellies, jams, and preserves. It is used in very large quantities to fill sole leather and tanning extracts, as a constituent of various sizes for ropes and textiles, and in chewing gum and chewing tobacco.

Grape sugar, corn sugar, is the name given to the crude *d*-glucose made on the large scale and used in the manufacture of vinegar, lactic acid, etc., and as a reducing agent, *e.g.* in dyeing with indigo and in silvering mirrors. It contains 70-86 per cent *d*-glucose and some of the carbohydrates intermediate between starch and *d*-glucose (dextrins, maltose, and isomaltose). It is not much used in food products on account of its bitter, unpleasant taste. The process of manufacture is the same as that for the preparation of glucose given above, except that more hydrochloric acid is used and the hydrolysis of the starch is carried further. When a sample of the liquid no longer gives a precipitate with alcohol, it is assumed that no dextrin is present, as dextrin is insoluble in alcohol. After neutralizing with sodium carbonate, filtering, and decolorizing with bone-char, the solution is concentrated in vacuum pans to the proper point and poured while hot into moulds. Grape sugar is a wax-like, solid mass of crystals of *d*-glucose hydrate ( $C_6H_{12}O_6 + H_2O$ ), white when fresh, but soon turning yellow and becoming extremely hard. Anhydrous grape sugar (dextrose), said to be 99 per cent pure *d*-glucose, is also made commercially and is the purest form of the sugar on the market.

*d*-Glucose exists in two stereoisomeric modifications which are designated as  $\alpha$ - and  $\beta$ -*d*-glucose. The  $\alpha$ -form is always obtained when *d*-glucose crystallizes from its aqueous solutions in the cold (as the hydrate,  $C_6H_{12}O_6 + H_2O$ ) or, in the anhydrous form, from a boiling saturated solution in alcohol. The anhydrous form of the  $\alpha$ -*d*-glucose is also obtained by crystallizing the concentrated aqueous solution at 30° to 35°. It crystallizes in needles or prisms, melting at 146°, and is soluble in three parts of water at 0°.  $\beta$ -*d*-Glucose is obtained when a concentrated aqueous solution of *d*-glucose is dried at 110°, the mass

then dissolved in an equal volume of water, and the solution quickly brought to crystallization by the addition of absolute alcohol with vigorous stirring. It forms microscopic crystals that melt at  $148^{\circ}$  to  $150^{\circ}$  and dissolve in 0.65 part of water at  $15^{\circ}$ . Both modifications show *mutarotation*, i.e. the rotation of the freshly prepared solution changes on standing or quickly on the addition of alkali until it becomes constant. The  $\alpha$ -form shows an initial specific rotation of  $+111.2^{\circ}$ , the  $\beta$ -form of  $17.5^{\circ}$ . On standing or on the addition of alkali, both forms show the same value,  $+52.3^{\circ}$ . In a solution of *d*-glucose, which gives this constant value, there is an equilibrium between the  $\alpha$  and  $\beta$ -forms, corresponding to 36.8 per cent  $\alpha$  and 63.2 per cent  $\beta$ .

The strength of a solution of *d*-glucose is usually determined in the polarimeter from its specific rotation. *d*-Glucose is about half as sweet as cane sugar and ferments with yeast or zymase, giving alcohol and carbon dioxide as the main products. The natural *d*-glucose is dextrorotatory. A *l*-glucose and a *dl*-glucose have been made synthetically from the corresponding *l'*- and *dl*-arabinoses:—



*l*-Glucose does not ferment with yeast, but otherwise it resembles *d*-glucose very closely except that it is levorotatory,  $-51.4^{\circ}$  after the solution has stood for some time. When oxidized, the glucoses give the gluconic acids,



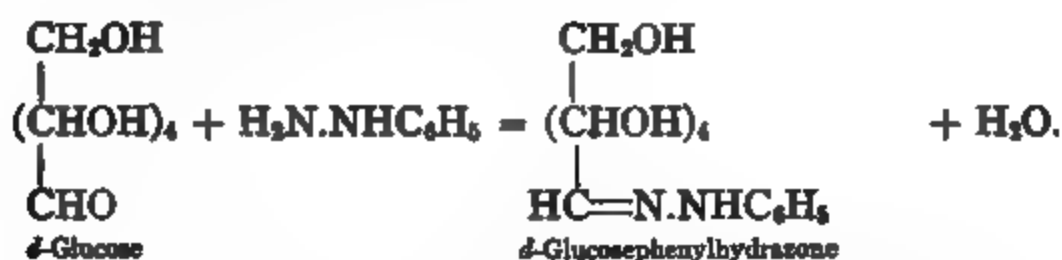
and then the saccharic acids,  $\text{HOOC}(\text{CHOH})_4\text{COOH}$  (206). As these acids have been proved to contain a normal carbon chain, it follows that the glucoses must be normal compounds and contain a primary alcohol group and an aldehyde group at the ends of the chain. On reduction the glucoses yield

the sorbitols,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$  (175) — another proof of the presence of the aldehyde group in them. Heated with acetic anhydride and zinc chloride, the glucoses give penta-acetates,

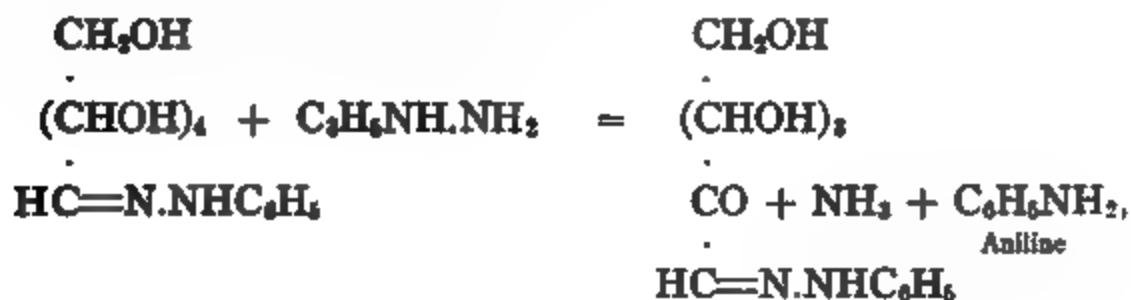


showing the presence of *five* alcohol groups. *d*-Glucose gives an oxime,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}=\text{NOH}$ , with hydroxylamine, reduces an ammoniacal solution of silver nitrate (forming a silver mirror), and reduces Fehling's solution on heating — reactions which are characteristic of aldehydes. The reaction with Fehling's solution is frequently made use of to detect the presence of *d*-glucose and to determine its amount. Fehling's solution is best made by dissolving 69.3 grams of crystallized copper sulphate in one liter of water, and then preparing a solution of 346 grams Rochelle salt and 200 grams of anhydrous soda in a liter of water. In using, equal volumes of the two solutions are mixed, and the mixture diluted with an equal volume of water. With this solution *d*-glucose can be shown to be present in solutions containing 0.00005 per cent of the sugar.

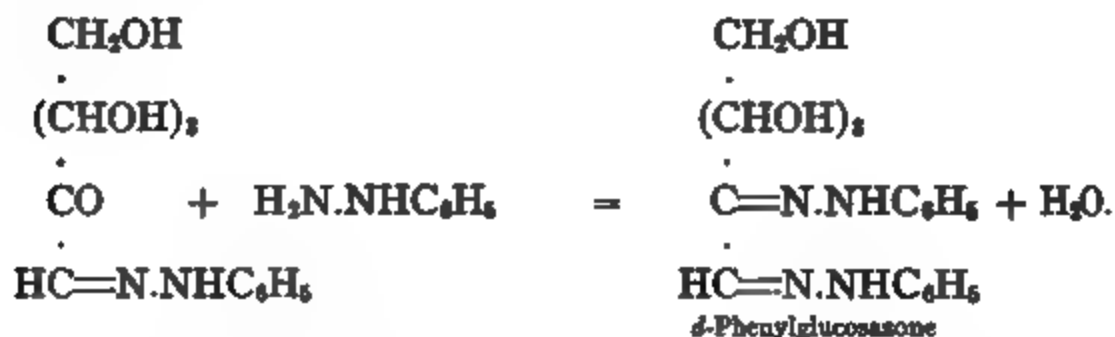
With phenylhydrazine *d*-glucose reacts, like all aldehydes, giving a phenylhydrazone: —



Heated with an excess of phenylhydrazine, the phenylhydrazone loses two hydrogen atoms, just as the phenylhydrazone of glyceric aldehyde (215) does: —



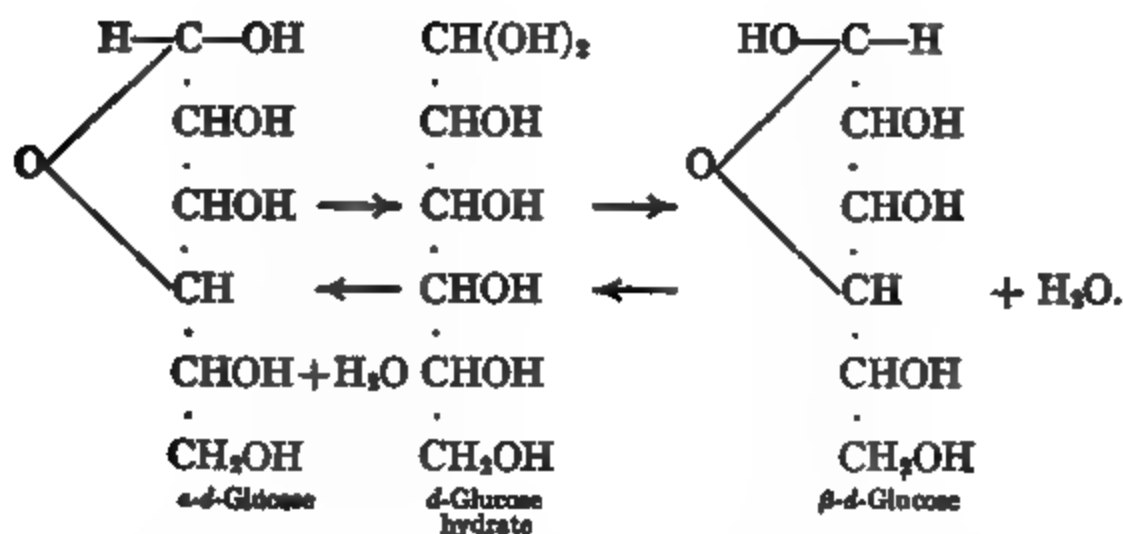
and the compound formed, which contains a *ketone* group, reacts with another molecule of phenylhydrazine to form *d*-phenylglucosazone: —



This *d*-phenylglucosazone is almost insoluble in water and this reaction can hence be used to show the presence of *d*-glucose in solutions. It crystallizes from dilute alcohol in yellow needles, that melt, when rapidly heated, at about 205°. Both *d*-mannose and *d'*-fructose give *d*-phenylglucosazone when heated with an excess of phenylhydrazine, and hence in testing solutions for *d*-glucose care must be taken to be sure that neither of these sugars is present.

*d*-Glucose, like all aldehydes, combines with hydrocyanic acid to form a cyanhydrin,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHOH.CN}$ . When this is hydrolyzed it gives a hexahydroxy-*n*-heptane acid,  $\text{CH}_2\text{OH}(\text{CHOH})_5\text{COOH}$ . On reduction with hydriodic acid and phosphorus this gives normal heptane acid,  $\text{CH}_3(\text{CH}_2)_5\text{COOH}$ . This is a proof both of the aldehyde group in *d*-glucose and of the normal structure, for *n*-heptane acid could not have resulted from a ketose or from an aldose containing an iso chain. (See Fructose.)

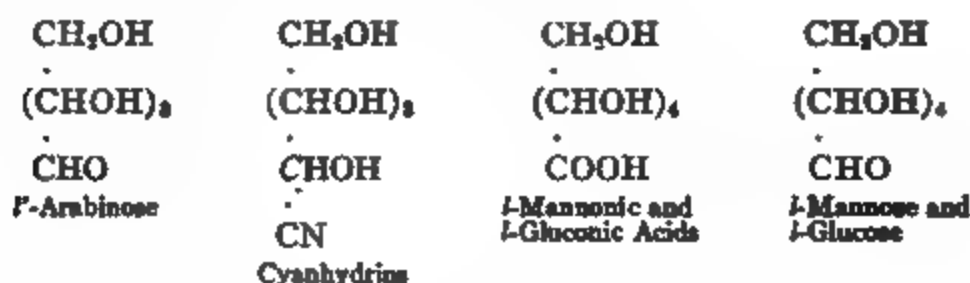
It has been shown that in aqueous solutions of *d*-glucose there are present in addition to the  $\alpha$ - and  $\beta$ -forms (222) small amounts of the aldehyde or the hydrate. This will account for the aldehyde reactions of *d*-glucose solutions and explain the transformation of the two forms of the *d*-glucose into each other: —



Glucose hydrate,  $\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O}$ , like chloral hydrate, contains two hydroxyl groups attached to the end carbon atom. When this loses water it can give either  $\alpha$ -glucose or  $\beta$ -glucose or both, compounds analogous to the  $\gamma$ -lactones (187). When these compounds are formed, the end carbon atom now becomes asymmetric, and hence two stereoisomers are formed. When  $\alpha$ -glucose goes over into  $\beta$ -glucose or the  $\beta$ -form into the  $\alpha$ -form, glucose hydrate is the intermediate product as shown above.

***d*-Mannose** occurs free in orange peel and in the combined state in some glucosides, but especially in the form of complex polysaccharoses, mannosans, it is very widely distributed in nature. It was first made by carefully oxidizing mannitol (hence the name), when it is obtained together with *d'*-fructose. (Compare with glycerose) It is best made from the ivory nut, so largely used in making buttons. The turnings and shavings, obtained as a waste product in the manufacture of buttons, are hydrolyzed with dilute mineral acid and the mannose precipitated from the solution with phenylhydrazine, as mannosephenylhydrazone, which, unlike glucosephenylhydrazone, is only slightly soluble in water. *d*-Mannose crystallizes in the rhombic system, melts at  $132^\circ$  and tastes sweet. It is readily fermented with yeast. It is partially converted into its isomers *d*-glucose and *d'*-fructose by the action of small quantities of alkalies, and these sugars are partially converted into mannose by the same reagent. Especially characteristic of *d*-mannose is its difficultly soluble phenylhydrazone,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}=\text{N.NHC}_6\text{H}_5$ . When heated with an excess of phenylhydrazine *d*-mannose gives the same phenylglucosazone that *d*-glucose or *d'*-fructose does. *d*-Mannose is dextrorotatory. A *l*-man-

nose and a *dl*-mannose have been prepared synthetically from *D*- and *dl*-arabinose: —



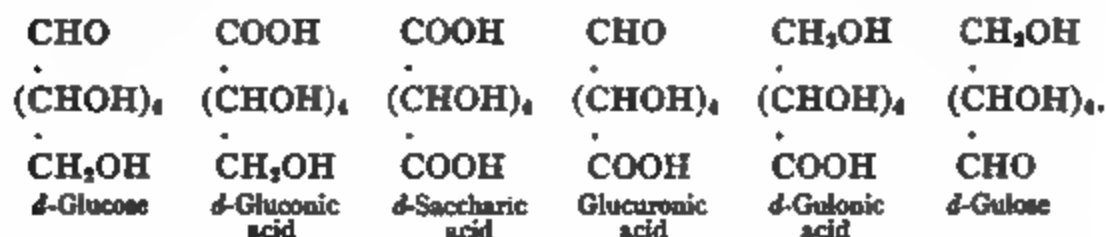
When hydrocyanic acid combines with *D*-arabinose two stereoisomeric cyanhydrins are formed as the carbon atom to which the cyanogen group attaches itself becomes asymmetric. On hydrolysis these two cyanhydrins give *L*-mannonic and *L*-gluconic acids, which are not optical antipodes, and hence may be separated from each other by crystallization of their lactones. When these lactones are reduced, *L*-mannose and *L*-glucose (223) are formed.

*L*-Mannose resembles its optical antipode very closely, except that it is not fermented by yeast. On oxidation the mannoses give mannonic acids and then the mannosaccharic acids. On reduction they give the mannitols (174).

**Galactoses.** — *D*-Galactose is found frequently in plants and animals in the form of polysaccharoses, galactans, and glucosides. It is a constituent of milk sugar (lactose) and of raffinose. It is usually prepared by the hydrolysis of milk sugar with dilute sulphuric acid. Like *D*-glucose it exists in two stereoisomeric modifications,  $\alpha$ - and  $\beta$ -. The  $\alpha$  form crystallizes from water with one molecule of water of crystallization, from alcohol in the anhydrous form. *D*-Galactose is dextrorotatory. The solution shows mutarotation. (See Glucose.) On oxidation *D*-galactonic and mucic acids are formed. On reduction dulcitol results. *D*-Galactose ferments with some yeasts, but more difficultly than *D*-glucose. It gives an oxime with hydroxylamine, which is difficultly soluble in cold water, and a phenylhydrazone with phenylhydrazine, which is also but slightly soluble in cold water. *L*-Galactose is obtained by fermenting *dl*-galactose with beer yeast, as it does not undergo fermentation. It is oxidized first to *L*-galactonic acid and then to mucic acid. On reduction it gives dulcitol. With phenylhydrazine it forms a phenylhydrazone rather difficultly soluble in water. *dl*-Galactose is made by the oxidation of dulcitol with hydrogen peroxide. It can be separated into its optical components by means of *d*-amylphenylhydrazine. On fermentation with beer yeast *L*-galactose is left in the solution.

The *guloses* are made from the *glucoses*, whence the name by reversing the order of the letters "lu." *D*-Gulose is obtained from

*d*-glucose by oxidizing it to *d*-saccharic acid and then reducing its lactone, forming the aldehyde acid, glucuronic acid. This on further reduction gives *d*-gulonic acid, the lactone of which reduces to *d*-gulose: —



It will be seen from this synthesis that the space arrangement of the groups around the four asymmetric carbon atoms must be the same in *d*-gulose as in *d*-glucose. The only difference is in the positions of the primary alcohol group and the aldehyde group. *d*-Gulose hence gives *d*-sorbitol on reduction and *d*-saccharic acid on oxidation just as *d*-glucose does.

It is known only in the form of a colorless syrup, which does not ferment with yeast. The *l*-gulose is made from *l*'-xylose:



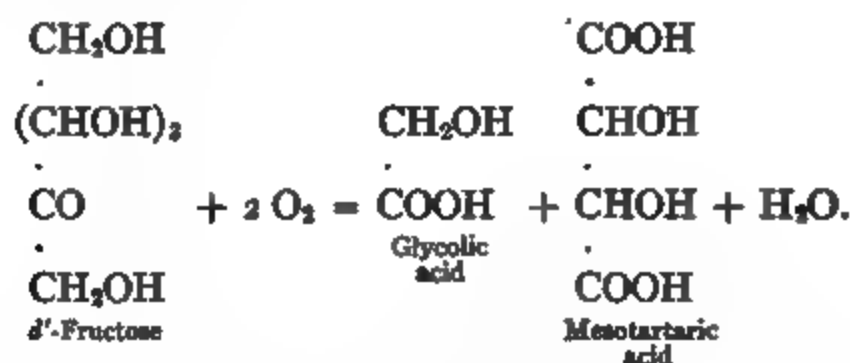
It is not fermentable with yeast, has a sweet taste and is levorotatory.

The other aldohexoses have been made in a similar manner from the pentoses, *d*-talose from *d*-lyxose, *d*'- and *l*'-idose from the xyloses, and allose and altrose from *d*'-ribose.

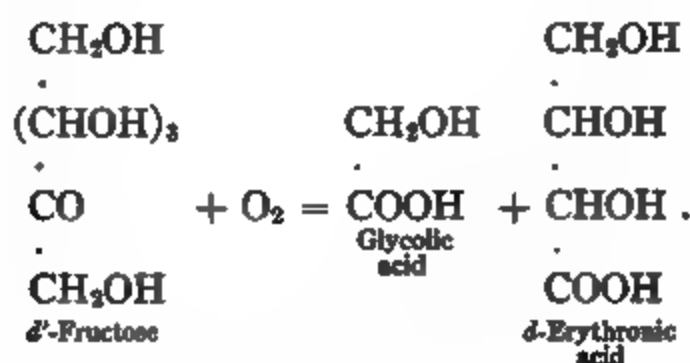
***d*'-Fructose (levulose)** is the most important ketose known. In the free condition it is very widely distributed in plants. Together with *d*-glucose it occurs abundantly in sweet fruits and in honey. It is a constituent of cane sugar and of raffinose and occurs also in certain starch-like compounds, *e.g.* in inulin of the dahlia root. It is formed in the hydrolysis of cane sugar, but is best prepared from inulin, as it is the only sugar formed in the hydrolysis of this carbohydrate. *d*'-Fructose reduces Fehling's solution more rapidly than any of the other natural sugars. *d*'-Fructose crystallizes from absolute alcohol in rhombic prisms, melting at 95°–105°, from concentrated aqueous solutions in needles with  $\frac{1}{2}$ H<sub>2</sub>O. It is said to be one and a half times as sweet as cane sugar. It is used in place of cane



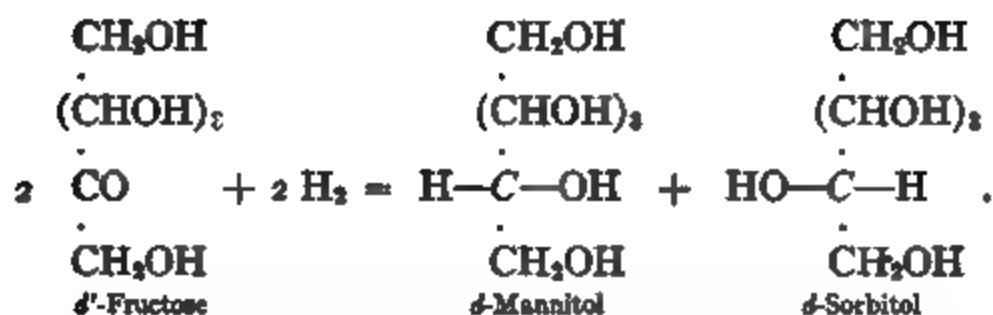
sugar by diabetics. It ferments with yeast as readily as *d*-glucose and is levorotatory. It is formed together with *d*-mannose by cautious oxidation of mannitol with nitric acid, while oxidation of mannitol with the sorbose bacteria gives *d'*-fructose alone. *d'*-Fructose is also formed by molecular rearrangement of *d*-glucose and of *d*-mannose by alkali. Considerable quantities of *d'*-fructose result from the action of strong sulphuric acid on *d*-glucose. When oxidized with dilute nitric acid *d'*-fructose gives glycolic acid, oxalic acid, and mesotartaric acid, but no saccharic acid (distinction from *d*-glucose): —



The oxalic acid results from the oxidation of some of the glycolic acid. When oxidized by mercuric oxide in the presence of a solution of barium hydroxide *d'*-fructose gives glycolic acid and *d*-erythronic acid: —

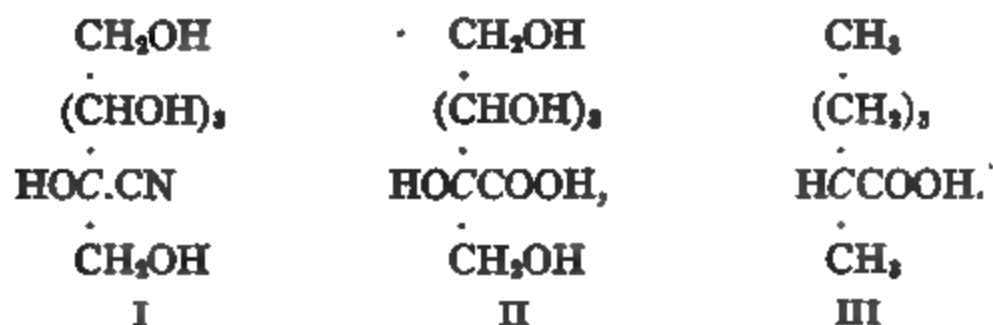


The formation of these products on oxidation shows that *d'*-fructose is a ketose having the above structure. On reduction also *d'*-fructose differs from *d*-glucose, as it gives equal amounts of *d*-mannitol and *d*-sorbitol, whereas *d*-glucose gives *d*-sorbitol only: —



It will be seen from the above formulas that, when the ketone group is reduced to the secondary alcohol group, the carbon atom italicized becomes asymmetric, and hence two stereoisomers are formed. This is another proof of the presence of the ketone group in *d'*-fructose.

*d'*-Fructose combines with hydrocyanic acid to give a cyanhydrin, I: —



When this is hydrolyzed it gives a hexahydroxyheptoic acid, II, isomeric with that obtained from glucose (225). When this acid is reduced with hydriodic acid and phosphorus it gives methyl-*n*-butylacetic acid, III, isomeric with the *n*-heptane acid obtained from glucose. It follows from this that *d'*-fructose must be a ketose having the above structure.

With hydroxylamine *d'*-fructose gives an oxime, isomeric with that obtained from *d*-glucose,

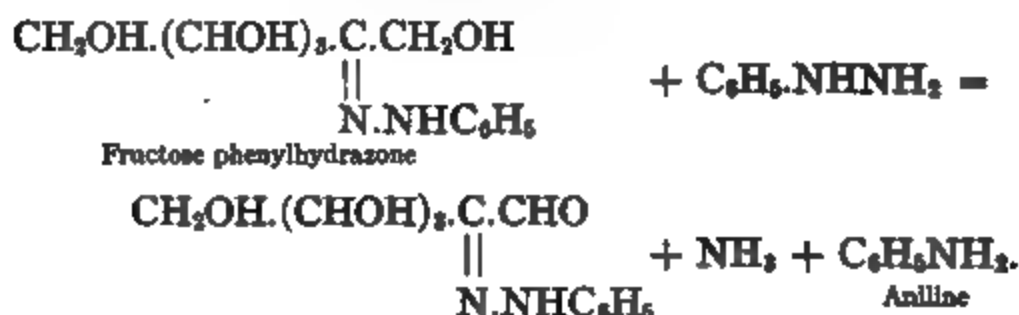


It also reacts with phenylhydrazine to give a phenylhydrazone,

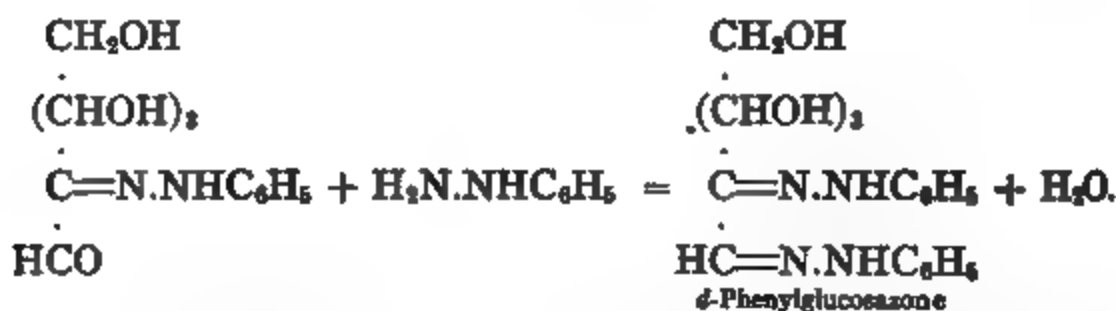


isomeric with that obtained from *d*-glucose. When heated

with an excess of phenylhydrazine, this phenylhydrazone loses two atoms of hydrogen from the primary alcohol group, converting it into an aldehyde group:—

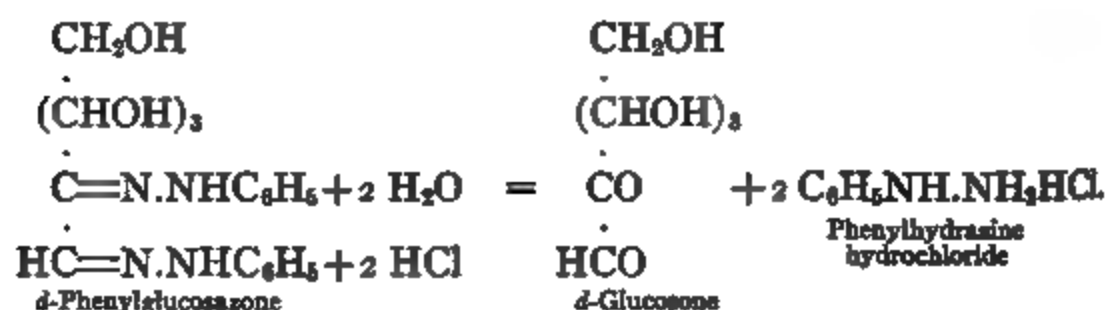


This compound then reacts with another molecule of phenylhydrazine to give *d*-phenylglucosazone:—



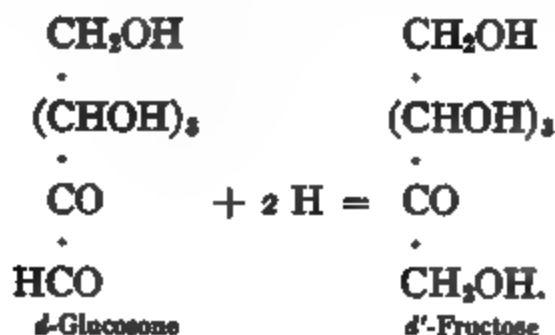
The *d*-phenylglucosazone thus obtained is identical with that formed by the action of an excess of phenylhydrazine on *d*-glucose or on *d*-mannose. It follows from this that the arrangement of the groups in space around the three asymmetric carbon atoms must be the same in fructose, glucose and mannose.<sup>1</sup>

When this *d*-phenylglucosazone is treated with fuming hydrochloric acid, the phenylhydrazine residues are split off, and a compound containing a ketone and an aldehyde group and hence called glucosone is formed:—



<sup>1</sup> For the methods used in the determination of the configuration of the sugars by Emil Fischer and others see *Stereochemistry*, by A. W. Stewart, page 50.

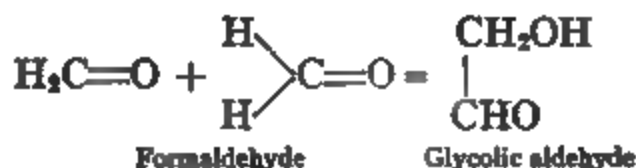
On reduction with zinc and acetic acid this *d*-glucosone gives *d'*-fructose: —



By means of these reactions, it will be seen that it is possible to convert *d*-glucose and *d*-mannose into *d'*-fructose. As *d'*-fructose gives both sorbitol and mannitol on reduction, and sorbitol on oxidation gives *d*-glucose, and mannitol *d*-mannose, it is also possible to obtain both *d*-glucose and *d*-mannose from *d'*-fructose. For this reason this fructose is called *d'*-fructose, although it is *levo*-rotatory. With methylphenylhydrazine *d'*-fructose gives a methylphenylglucosazone more readily than *d*-glucose does.

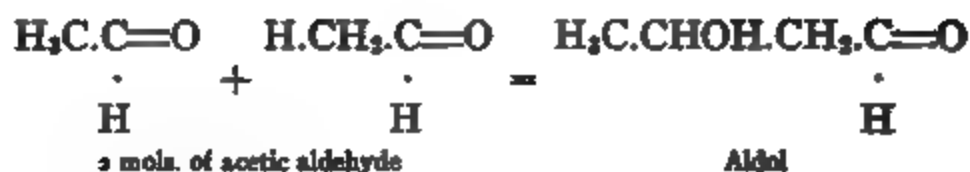
***dl*-Fructose** is of great historical interest, as it was the first sugar prepared synthetically, and from it the sugars occurring in nature have been obtained. It has been made: —

(1) By the condensation of formaldehyde with bases (formose). In this synthesis it is probable that the aldehyde of glycolic acid is first formed by the condensation of two molecules of formaldehyde: —



and that this undergoes further condensation to the hexose. (See below.)

This condensation is called the *aldol condensation*, as the product formed is an *aldehyde alcohol*. Aldol itself is obtained by the condensation of two molecules of acetic aldehyde with bases: —



From the above formula it will be seen that it is  $\beta$ -hydroxybutyric aldehyde, and that it is not a sugar, as it does not contain the group,  $\text{—CHOH—CO—}$ . This aldol condensation is very important, and it has been suggested that the sugars occurring in nature are built up in plants by its means from formaldehyde, formed by the action of the green coloring matter of plants (chlorophyll) and water, in the presence of sunlight, on the carbon dioxide of the air:—

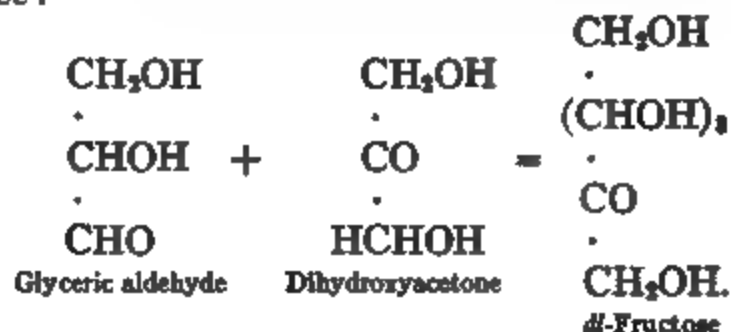


It is well known that green plants take up carbon dioxide from the air and set free an equal amount of oxygen.

(2) The second method of preparing *dl*-fructose artificially starts with acrolein,  $\text{CH}_2\text{=CH.CHO}$ . This takes up bromine, forming acrolein dibromide,  $\text{CH}_2\text{Br.CHBr.CHO}$ , which with barium hydroxide gives glyceric aldehyde,



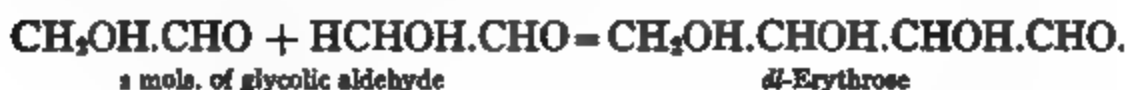
It has already been shown that alkalies transform aldoses into ketoses, and it is believed that the barium hydroxide converts a part of the glyceric aldehyde into dihydroxyacetone. These two substances then undergo the aldol condensation and form *dl*-fructose:—



The sugar thus obtained from *acrolein* was first called *α-acrose* by Emil Fischer before he had proved it to be identical with *dl*-fructose.

(3) The third method of synthesis, also due to Emil Fischer, depends on the aldol condensation of a mixture of glyceric aldehyde and dihydroxyacetone, *glycerose*, obtained by the oxidation of glycerol.

(4) The fourth method depends on the aldol condensation of glycolic aldehyde,  $\text{CH}_2\text{OH}\cdot\text{CHO}$ , which is regarded by some chemists as the simplest sugar, as it gives all the reactions characteristic of the aldoses and has a sweet taste. It undergoes the aldol condensation with dilute alkalies, even at  $0^\circ$ , and gives *dl*-erythrose and  $\alpha$ -acrose:—



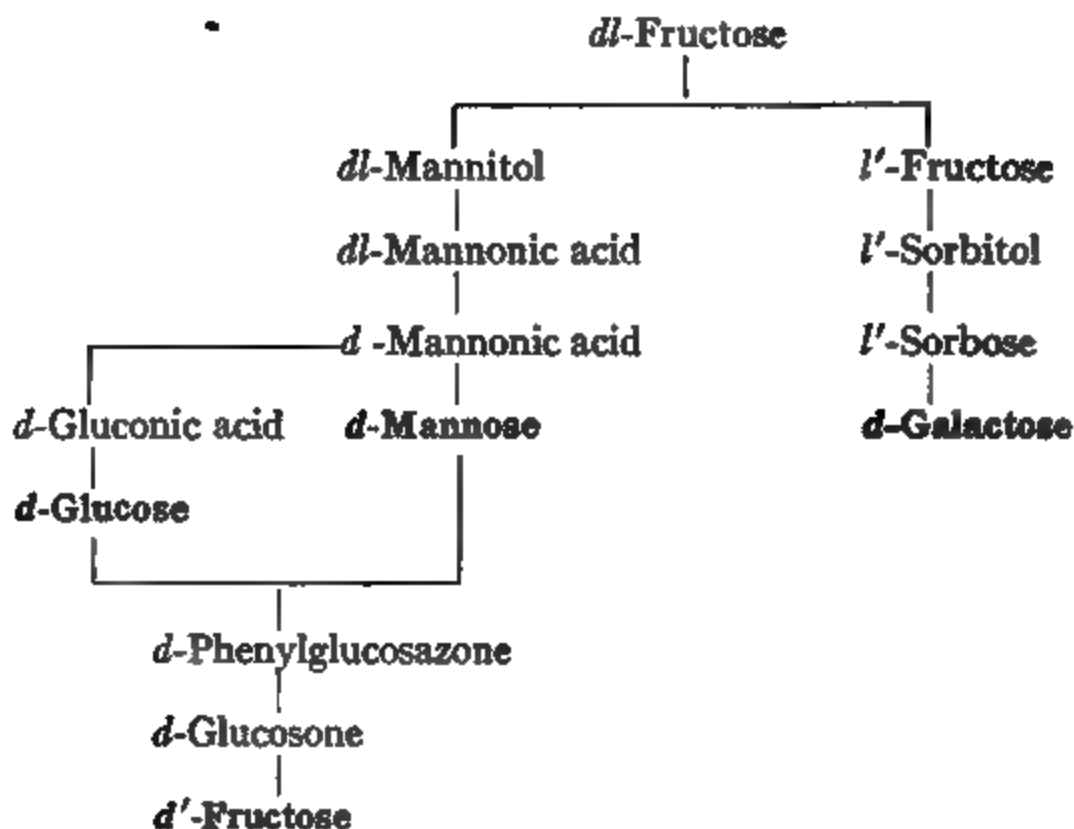
If the erythrose then undergoes molecular rearrangement under the influence of the alkali into erythrulose, and this undergoes the aldol condensation with the glycolic aldehyde,  $\alpha$ -acrose results:—



*l'*-Fructose is obtained by fermenting the *dl*-fructose with yeast, as only the *d'*-fructose undergoes fermentation.

**Synthesis of the sugars (hexoses) occurring in nature.**—The *dl*-fructose on reduction gives *dl*-mannitol, which on oxidation is converted into *dl*-mannonic acid. This can be separated into its optically active isomers, and the *d*-mannonic acid lactone gives *d*-mannose on reduction. *d*-Mannonic acid when heated with quinoline is partially converted into *d*-gluconic acid, and this gives *d*-glucose when its lactone is reduced. From both *d*-mannose and *d*-glucose, *d*-phenylglucosazone is obtained, and from this by the method given above *d'*-fructose is made.

*l'*-Fructose (see above) gives *l'*-sorbitol on reduction. When this is oxidized with the sorbose bacteria, *l'*-sorbose, stereoisomeric with *d'*-fructose, results. This undergoes molecular rearrangement with alkalies, giving *d*-galactose. The following scheme gives these results in outline:—



Thus all the hexoses occurring in nature have been made synthetically, and this is justly regarded as one of the greatest achievements of modern chemistry.

#### POLYSACCHAROSES, POLYPOSES OR COMPLEX SUGARS

These sugars either occur in nature, *e.g.*, cane sugar and sugar of milk, or are made from the more complex natural carbohydrates, as maltose (malt sugar) from starch by the action of diastase. Their most characteristic property is that they undergo hydrolysis when heated with dilute mineral acids or under the influence of certain enzymes into the monosaccharoses or monoses. Thus cane sugar gives *d*-glucose and *d'*-fructose; milk sugar gives *d*-glucose and *d*-galactose; and malt sugar gives two molecules of *d*-glucose. These sugars are hence called disaccharoses or hexodioses.

**Raffinose**<sup>1</sup> is an example of a *trisaccharose* or *hexotriose*, as it gives three monoses (hexoses) on hydrolysis with dilute mineral acids: —

<sup>1</sup> Raffinose resembles sucrose very closely in its properties, but is tasteless.



Crystalline tetra-, penta-, and hexasaccharoses are also known. All these complex sugars have the general formula,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n + \text{H}_2\text{O}$ , *e.g.*, disaccharoses  $(\text{C}_6\text{H}_{10}\text{O}_5)_2 + \text{H}_2\text{O}$ , trisaccharoses  $(\text{C}_6\text{H}_{10}\text{O}_5)_3 + \text{H}_2\text{O}$ , tetrasaccharoses  $(\text{C}_6\text{H}_{10}\text{O}_5)_4 + \text{H}_2\text{O}$ , etc.

Owing to the ease with which they are hydrolyzed to monoses, the complex sugars are regarded as anhydrides of the hexoses. The hexodioses are the most important of these sugars. They are neutral, colorless compounds having a sweet taste, readily soluble in water and crystallize better than the monosaccharoses.

Cane sugar, beet sugar, sucrose, saccharose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , is the most important of all the sugars and the one which has been longest known. When the term sugar alone is used it always refers to this compound. The production and refining of this sugar has become one of the great modern industries. Its importance as a food is shown by the fact that the world's production in 1920-1921 is estimated to be over 17,000,000 long tons, of which slightly over one quarter is beet sugar, the rest cane sugar. Cane sugar occurs extensively distributed in plants and plays a very important part in the metabolism of plants. It is found, always in the free condition, in sorghum, in certain palms, in the sugar maple, in coffee, walnuts, and other nuts, in the blossoms of plants and in honey. It occurs especially abundantly in sugar cane (about 14.5 per cent) and in the sugar beet (16-20 per cent) and these two plants supply practically all the world's sugar, though a small quantity is made from the sugar maple (maple sugar).

When sugar cane is used, it is crushed and mixed with water to extract all the sugar. The juice is then filtered, treated with lime and heated to the boiling point to remove acids (which would hydrolyze the cane sugar), proteids, coloring matters, and other impurities. After filtering, the purified juice is sometimes bleached with sulphur dioxide and the faintly alkaline juice is concentrated in vacuum evaporators to a syrup. This is then further concentrated in vacuum pans till the sugar



begins to crystallize. The crystals of sugar are separated from the mother liquor by means of centrifugals, which are rapidly revolving fine sieves. These retain the crystals, but expel the mother liquor by centrifugal force. After washing in the centrifugals with a small quantity of water to remove the adhering molasses, the crystals are dried.

When sugar beets are used, the juice is extracted by the diffusion process. The beets are sliced and loosely packed in the cells of the diffusion apparatus through which hot water circulates in such a manner that fresh water comes into contact with the nearly exhausted beets. This dilute sugar solution then passes into the next cell containing partially exhausted beets, and so on, until finally the fresh beets are extracted with the strongest sugar solution. The cell walls of the beets allow the sugar to diffuse through, but hold back colloidal substances. The juice is first treated with lime and then with carbon dioxide to remove most of the lime, filtered, decolorized with sulphur dioxide, and then concentrated as described above.

Considerable sugar is left in the molasses, and this is recovered in part by precipitating the sugar as tribasic calcium saccharate,  $C_{12}H_{22}O_{11} \cdot 3CaO$ , which is then decomposed by carbon dioxide and the filtrate concentrated for the crystallization of the sugar.

Cane sugar factories produce a large quantity of molasses, which is utilized as a table syrup, in making alcohol, and in baking.

Beet sugar molasses is unfit for human food on account of its impurities and disagreeable taste. It is used in making alcohol and as cattle food.

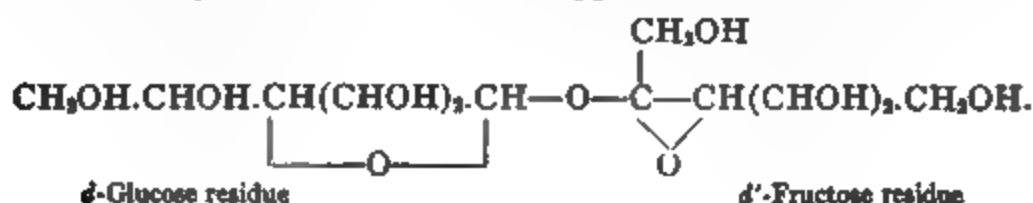
The raw sugar obtained as described above contains about 96 per cent sucrose. It is colored and contains impurities and must be further refined before it is used as a food. This is done in sugar refineries. The raw sugar is treated with a small quantity of water or with dilute sugar solution. This removes most of the impurities and leaves the crystals. These are separated from the syrup by means of centrifugals, dissolved in water, and the solution treated with lime. The excess of lime and the cal-

cium salts are then precipitated with mono calcium phosphate or phosphoric acid as calcium phosphate and the solution filtered. It is then decolorized with sulphur dioxide or bone black and concentrated in vacuum pans to crystallization. The white sugar of commerce is extraordinarily pure. It contains at least 99.0 per cent sucrose.

Sucrose crystallizes in the monoclinic system. It is very soluble in water, but difficultly soluble in alcohol. It melts at about  $160^{\circ}$  and then solidifies to an amorphous glass-like mass. When more strongly heated it turns brown, undergoes decomposition, and forms a mixture of substances called *caramel* much used in making confectionery. Heated still higher it carbonizes, forming sugar charcoal, and gives off gases. Sucrose does not reduce Fehling's solution, is not changed by the action of dilute alkalis, and does not react with phenylhydrazine. The aqueous solution is dextrorotatory ( $[\alpha]_D^{20} = +66.5^{\circ}$ ), and it does not show mutarotation (223). When hydrolyzed with dilute mineral acids or with the enzyme, invertase, sucrose gives a mixture of equal parts of *d*-glucose and *d'*-fructose. As *d'*-fructose is very much more strongly levorotatory ( $-93^{\circ}$ ) than *d*-glucose is dextrorotatory ( $+52.3^{\circ}$ ) the mixture is levorotatory. For this reason it is called invert sugar and the term "inversion" is used for the hydrolysis of the disaccharoses into monosaccharoses. Cane sugar does not undergo fermentation directly, but only after hydrolysis into glucose and fructose. Most of the varieties of yeast produce the enzyme, invertase, which hydrolyzes the cane sugar, and the glucose and fructose then ferment. Cane sugar is twice as sweet as *d*-glucose, but it is not as sweet as *d'*-fructose.

Cane sugar gives an *octaacetate*,  $C_{12}H_{14}O_8(OCOCH_3)_8$ , with acetic anhydride. This melts at  $67^\circ$  and has a bitter taste.

It also forms an octamethyl derivative,  $C_{12}H_{14}O_8(OCH_3)_8$ . The following formula has been suggested for sucrose:—



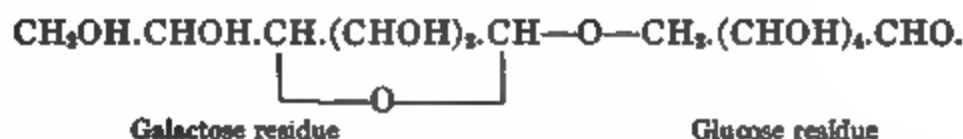
It is in accord with the fact that sucrose contains *eight* hydroxyl groups, does not reduce Fehling's solution nor react with phenylhydrazine (no longer contains a carbonyl group), and undergoes hydrolysis so readily and quantitatively into *d*-glucose and *d'*-fructose.

Sucrose has not yet been made synthetically.

To determine cane sugar quantitatively, in raw sugars for example, use is made of its property of rotating the plane of polarized light. The rotation is determined in a polariscope (saccharimeter) having a scale which enables the percentage of sugar to be read directly. The inversion of cane sugar is brought about by an extremely small amount of acid; thus when a mixture of 80 parts of sugar and 20 parts of water containing only 0.005 per cent hydrochloric acid is digested in boiling water for one hour, it is almost completely hydrolyzed. The inversion is a catalytic phenomenon and is due to the hydrogen ions of the acid. Since it has been found that the inversion constant and the hydrogen ion concentration are proportional, the velocity of inversion of cane sugar is used to determine the strength of acids. The rate of hydrolysis of sucrose is 1000 times more rapid than that of lactose or maltose.

Sugar of milk, lactose,  $C_{12}H_{22}O_{11} + H_2O$ , is found in the milk of all mammals, and it is the only sugar present in this secretion. It does not occur in plants. It is prepared by the evaporation of the whey, which is the fluid left when the casein and the fat of skimmed milk are precipitated by rennet in making cheese. It is purified by recrystallization from water. It dissolves in 6 parts of cold water and  $2\frac{1}{2}$  parts of hot water. It crystallizes from water at ordinary temperatures with a molecule of water of crystallization, but, if crystallized from water above  $95^\circ$ , the crystals contain no water. It is about one fourth as sweet as cane sugar. Like *d*-glucose it exists in an  $\alpha$ - and a  $\beta$ -form and shows mutarotation, due to the formation of a mixture of these two forms in equilibrium ( $[\alpha]_D^{20} = +55.3^\circ$ ). On long boiling with dilute mineral acids lactose is hydrolyzed to *d*-glucose and *d*-galactose. This same effect is produced by the enzyme, *lactase*, which is present in certain varieties of yeast (*torula*) and

in the intestines of the calf. It is not hydrolyzed by invertase, nor will lactase hydrolyze cane sugar. Lactose is not fermented by beer yeast, as this yeast contains no *lactase*. It is fermented by certain microorganisms (*torulæ*), which produce lactase. Milk sugar is converted very readily into lactic acid by a number of bacteria. It reduces Fehling's solution, forms a silver mirror with an ammoniacal solution of silver nitrate, and gives a phenyllactosazone with phenylhydrazine, which is soluble in boiling water. It gives an octaacetate with acetic anhydride. When oxidized with bromine water it gives a monobasic acid, *lactobionic acid*, containing twelve carbon atoms, and hence it must contain an *aldehyde* group. When lactobionic acid is hydrolyzed by mineral acids it gives gluconic acid and galactose, thus proving that the aldehyde group in lactose must be in the glucose residue. The following formula has been suggested for lactose:—



Lactose is used in the manufacture of pharmaceutical preparations and as a food.

**Maltose, malt sugar**,  $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O}$ , is formed from starch by the action of malt diastase. Other enzymes, such as the ptyalin of the saliva and the amylopsin of the pancreatic juice, also convert starch into maltose. Maltose also results from the hydrolysis of glycogen by enzymes. It crystallizes in needles containing one molecule of water and is readily soluble in water. Its solution shows upward mutarotation, *i.e.*, the rotation increases, as the equilibrium value ( $[\alpha]_D^{20} = +137^\circ$ ) is greater than the initial value. It reduces Fehling's solution and is easily decomposed by alkalies. It is completely fermented by beer yeast. This is due to the presence in the yeast of the enzyme, maltase, which hydrolyzes the maltose to two molecules of *d*-glucose, which then ferment. Dilute mineral acids also hydrolyze maltose to *d*-glucose, but not as readily as cane sugar. The other enzymes, invertase, diastase, lactase, etc.,

are without action on maltose. It reacts with phenylhydrazine to form a phenylmaltosazone and on oxidation with bromine water gives maltobionic acid, a monobasic acid, containing<sup>1</sup> 12 carbon atoms. This acid when hydrolyzed with mineral acids gives *d*-glucose and *d*-gluconic acid, and hence maltose must contain an aldehyde group. Maltose gives an octaacetate with acetic anhydride, and hence contains 8 hydroxyl groups. It is probably *stereoisomeric* with lactose (238) and has the same structural formula.

Maltose is the intermediate product in the manufacture of ethyl alcohol from corn, potatoes, and other materials consisting largely of starch. The starch is converted into maltose by the action of the diastase of malt, and the maltose is hydrolyzed by the maltase of the yeast to glucose, which then undergoes fermentation by the zymase of the yeast to alcohol and carbon dioxide.

**Isomaltose** is the name given by Emil Fischer to a disaccharose obtained by him by the action of strong hydrochloric acid on *d*-glucose. It does not ferment with yeast. It is probably identical with the disaccharose called revertose obtained by the synthetical action of maltase on *d*-glucose. It is not hydrolyzed by maltase or invertase, but gives *d*-glucose with emulsin.

#### COLLOIDAL<sup>1</sup> POLYSACCHAROSES

The carbohydrates belonging to this group, of which starch and cellulose are the most important members, are amorphous, tasteless, and, for the most part, insoluble substances, which are hydrolyzed to monoses by the action of dilute mineral acids. They belong to the class of compounds known as *colloids*. The composition of those regarded as anhydrides of the hexoses is expressed by the formula  $(C_6H_{10}O_5)_x$  or  $(C_6H_{10}O_5)_x + H_2O$  (235). The molecular weight is unknown, but is undoubtedly very large.

<sup>1</sup> By "colloidal" polysaccharoses is understood polysaccharoses which are insoluble in water (cellulose) or which form pseudo solutions in this solvent (starch, inulin, etc.). See *Applied Colloid Chemistry*, by W. D. Bancroft.

**Starch** ( $C_6H_{10}O_5$ )<sub>n</sub> or  $(C_6H_{10}O_5)_n + H_2O$ , is found in the form of granules having an organized structure in many different organs of green plants, particularly as a *reserve material*. Hence it is found especially abundantly in tubers, roots, nuts, and cereals, e.g., in all kinds of grain (wheat, Indian corn, etc.), in the potato, in chestnuts, and in acorns. The form and size of the starch granules are characteristic of the different plants, and it is frequently possible to identify the origin of a starch by a microscopic examination. In this country starch is generally made from Indian corn (maize) and in Europe from potatoes. Indian corn contains 55 per cent starch. About forty million bushels of shelled corn are used annually in making starch and products derived from starch (glucose, dextrans, malt syrup, etc.). The separation of the starch from the corn is largely mechanical. The corn is first soaked in warm water containing some sulphur dioxide and when soft enough is passed through a mill in order to break it up. The germ at the apex of the kernel which contains most of the oil is removed by passing the mass mixed with water through the germ separators. The semifluid mass is then ground and passed over sieves of bolting cloth, which allow the starch and gluten in suspension in water to pass through but retain the bran. The starch liquor is allowed to settle in troughs to free it from the lighter gluten. The starch is then washed several times with water by decantation, drained on wooden frames having cloth bottoms, and dried in kilns.

In polarized light starch grains are doubly refracting. Air-dried starch contains 10 to 20 per cent water. It can be obtained free from water by gradually drying at increasing temperatures up to  $109^{\circ}$ – $110^{\circ}$ . Starch is practically insoluble in cold water. When heated with water the starch grains swell, burst and form starch paste. If starch is treated with cold, dilute mineral acid for some days it is converted into *soluble starch*. This dissolves in hot water, forming a solution that is strongly dextrorotatory. Soluble starch is also formed by treatment with oxidizing agents or with alkalis. It is really a partially hydrolyzed starch and not a modification of

starch, as the name suggests. Starch is especially characterized by the blue color that it gives with iodine dissolved in a solution of potassium iodide. This reaction is used to identify starch granules in plants. Starch paste and soluble starch also give this reaction. It is apparently not due to the formation of a chemical compound of starch and iodine nor to the formation of a solid solution of iodine in starch, but is merely an adsorption phenomenon. The iodine is adsorbed by the starch. Starch forms nitrates with a mixture of nitric and sulphuric acids (nitrostarch used as an explosive) and acetyl derivatives with acetic anhydride.

The most important transformation of starch is its hydrolysis by boiling with dilute mineral acids. d-Glucose is the only monosaccharose formed in this hydrolysis, and under the proper conditions the starch can be nearly quantitatively converted into glucose. The hydrolysis of starch by the diastase of malt gives maltose, and under the proper conditions this transformation can be made nearly quantitative. Starch can be determined quantitatively by converting it into glucose by the action of dilute acids and determining the amount of sugar formed. Starch as it is obtained technically is not an individual compound, but is a mixture of several substances. The cell walls of the starch grains consist of *amylopectin*, while the contents of the cell form the *amylose*. Starch paste is essentially a solution of amylose thickened by undissolved mucilaginous amylopectin. Amylose, which forms the larger part of starch, is itself a complex mixture of closely related substances that differ in solubility in water. The so-called soluble starch is the lowest member of this series. In all its forms amylose is soluble in alkaline fluids without forming a paste. Even with warm water it never forms a paste. The amylose in solution gives a pure blue color with a solution of iodine, but the pure solid amylose does not. That starch and the dried starch paste give a blue color with iodine, is due to the fact that amylose is present in these substances, in the form of a solid solution. Amylose is only attacked by diastase when it is in solution, and on hydrolysis with diastase gives *maltose alone without perceptible forma-*

*tion of dextrins.* The amylopectin which forms the smaller part of the starch substance is also apparently not homogeneous. It swells with warm water and forms a mucilaginous paste and when superheated with water it gives a sticky solution. With a solution of iodine it gives a blue-violet color which is less intense than the blue color with amylose. The dextrins formed together with maltose by the action of diastase on starch are apparently derived from the amylopectin.

Starch is of very great importance as a large constituent of our food (bread, potatoes, cereals, etc.). In the stomach and intestines starch is hydrolyzed to maltose and glucose by the enzymes present in the digestive juices. It is much used as an adhesive paste and in laundries for stiffening clothes. In this process the starch is converted into dextrin by the hot iron. Starch is also the material from which commercial glucose (starch sugar) and the dextrins are made.

**Dextrins** are made from starch either by heating this to  $180^{\circ}$ – $200^{\circ}$  or by first moistening the starch with hydrochloric or nitric acid and then gently heating it. It forms a white or yellow powder and is used as an adhesive, especially for envelopes and postage stamps. The dextrins form colloidal solutions in water, but are insoluble in absolute alcohol. As the name indicates they are dextrorotatory ( $[\alpha]_d$  up to about  $+200^{\circ}$ ). They are completely converted into maltose by malt extract and into *d*-glucose by the action of dilute acids. Apparently there are several dextrins, some of which give a reddish-violet color with a solution of iodine (erythrodextrin) while others give no color (acchroödextrin). Some reduce Fehling's solution, others do not. Dextrin, also known as British gum, is used as a substitute for natural gums.

**Inulin**,  $(C_6H_{10}O_5)_x + H_2O$ , is a reserve material resembling starch, found in dahlia bulbs, chicory roots, etc. It forms a white hygroscopic powder, consisting of doubly refracting spherocrystals, which is very soluble in warm water (forming a colloidal solution). It is levorotatory ( $[\alpha]_d$  from  $-33^{\circ}$  to  $-40^{\circ}$ ) and gives no color with a solution of iodine. Dilute acids hydrolyze it more readily than starch, giving only *d'*-fructose.



It is also hydrolyzed to *d'*-fructose by the enzyme, inulase, but is not acted upon by diastase or the pancreatic juice.

**Glycogen (liver starch)**,  $(C_6H_{10}O_5)_n + H_2O$ , is a reserve material found in all developing cells of the animal organism, and is especially abundant in the liver. It also occurs, in small quantity, in the muscular tissue of animals, in yeast, and in mushrooms. It is usually prepared from fresh liver. When pure it forms a white, tasteless, and inodorous amorphous powder, which dissolves in water, forming an opalescent colloidal solution. This solution is dextrorotatory ( $[\alpha]_d = +196^\circ-197^\circ$ ) and gives a yellowish-brown to red-brown color with a solution of iodine. It is converted almost completely into *d*-glucose by the action of dilute acids, though it is not attacked even by strong alkaline solutions. It is also hydrolyzed by the ptyalin of the saliva, yielding maltose, and gives maltose and *d*-glucose with liver extract.

**Cellulose**,  $(C_6H_{10}O_5)_n$ , or  $(C_6H_{10}O_5)_n + H_2O$ . — Cellulose is the chief constituent of the cell walls of plants. It also occurs in the animal kingdom. Thus the tunica of the *Ascidia* is chiefly cellulose. It is usually prepared from cotton, which is 85 per cent cellulose, by extracting it with water, alcohol, ether, dilute alkalies, and acids, as cellulose is insoluble in all these solvents. This cotton cellulose is the only variety that has been carefully investigated, and the properties ascribed to cellulose are those observed in a study of this product. Absorbent cotton and filter paper are usually regarded as the purest form of cellulose, although they contain small amounts of impurities and, on account of the energetic treatment to which they have been subjected in order to purify them, cannot be regarded as entirely unchanged cellulose. Cellulose is strongly double refracting and behaves as a typical colloid, exhibiting the phenomena of swelling and adsorption. Air-dried cellulose contains 6 to 8 per cent of water, which may be removed by drying in a vacuum. It dissolves in Schweitzer's reagent, which is a solution of copper oxide in ammonia, and also in a strong solution of zinc chloride. Pure cellulose gives a yellow or brown color with a solution of iodine and this becomes blue

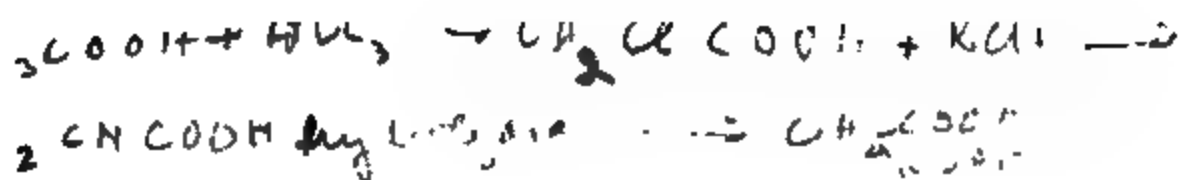
in the presence of concentrated sulphuric acid. It also gives a blue color with iodine dissolved in a solution of potassium iodide and containing zinc chloride, and this reaction is used as a test for cellulose. Cellulose dissolves in strong sulphuric acid (showing the presence of hydroxyl groups). If the solution is allowed to stand until it gives no precipitate when diluted with water, and the very dilute solution is heated in an autoclave to  $120^{\circ}$ , the cellulose is completely hydrolyzed to *d*-glucose. When heated with acetic anhydride, acetic acid, and some sulphuric acid (acetolysis), cellulose gives an octaacetate of the disaccharose  $C_{12}H_{22}O_{11}$ , called *cellubiose*, from which the sugar itself is obtained by saponification with alkali. This cellubiose bears to cellulose very much the same relation that maltose bears to starch. Like maltose it gives only *d*-glucose when hydrolyzed with dilute mineral acids. Cellulose, like starch, is therefore an anhydride of *d*-glucose. It is apparently very much more complex than starch, and probably has a much greater molecular weight. With acetic anhydride it gives a triacetate,  $(C_6H_7(OCOCH_3)_3O_2)_n$ , showing that it contains three alcoholic hydroxyl groups. A cold concentrated solution of sodium hydroxide (30 per cent) converts cellulose into cellulose hydrate. The alkali causes a shrinking of the fiber and combines with it to form an alcoholate. The alkali is afterwards removed by washing with water. This "mercerized" cotton, as it is called after Mercer who introduced the method into the textile industry, has a much greater attraction for dyestuffs and gives deeper shades than can be obtained with the unmercerized cotton. It also gives a silk-like finish to the cotton. Cold concentrated sulphuric acid produces a somewhat greater change in the cellulose (hydrolysis). Upon this change depends the manufacture of parchment paper. Unsized paper is dipped into 80 per cent sulphuric acid for 15 to 20 seconds and then freed from the acid by washing with water. The pores of the paper become filled with a gelatinous decomposition product of the cellulose, which makes it tougher and less porous. Parchment paper is colored blue-black by a solution containing iodine and potassium iodide (amyloid). Cellulose is the chief

constituent of the vegetable textile fabrics (cotton, linen, hemp and jute) and also of paper.

**Cellulose nitrates, nitrocellulose.** — Cellulose is converted into nitrates (nitrocellulose) by the action of a mixture of nitric and sulphuric acids. The lower nitrates (10 per cent to 12 per cent nitrogen, soluble in ether-alcohol) are called collodion cotton, soluble cotton, etc., while the higher nitrates (about 13 per cent nitrogen) are known as gun cotton. Celluloid is a solid solution of collodion cotton and camphor, which is used for manufacturing many articles formerly made from horn or ivory. Its chief use, however, is for photographic films, especially motion picture films. *Gun cotton* is used as a high explosive for filling torpedoes and bombs and also, when properly gelatinized, in the manufacture of *smokeless powders*.

**Cellulose acetate**, soluble in chloroform and also in a mixture of acetic ether and alcohol, forms a plastic mass with camphor resembling celluloid and is used in making motion picture films which are non-inflammable. It is a mixture of the di- and tri-acetates. It is also used in making artificial silk. *Artificial silk* is made by forcing solutions of cellulose or its esters through fine openings into a bath which coagulates the thread. This is then dried and wound on spools. Collodion cotton in solution in ether-alcohol was first used, the threads being "denitrated" in a bath of sodium hydrosulphide (*Chardonnet silk*). Another method makes use of a solution of cellulose in copper-oxide-ammonia. The blue solution is spun into a bath of dilute sulphuric acid which coagulates the threads and removes the copper (*Glanzstoff*). The latest method, which has superseded the other two, starts with a solution of *viscose* made by the action of sodium hydroxide and carbon bisulphide on cellulose. This solution contains the sodium salt of a cellulose xanthic acid ( $C_6H_5O_4.O.CS.SH$ , simplest formula). It is coagulated by being spun into a bath containing sodium bisulphate. Over eight million pounds of viscose silk were made in the United States in 1919.<sup>1</sup>

<sup>1</sup> For further information concerning the Cellulose Industries and the Manufacture of Paper see *Industrial Chemistry*, edited by Allen Rogers, 3d ed., 1920, and *Technology of Cellulose Esters*, by E. C. Worden, 1921.



## CHAPTER XII

### MIXED COMPOUNDS CONTAINING NITROGEN

IN connection with the preparation of dibasic acids from monobasic acids, reference was made to cyanacetic and the two cyanpropionic acids. These are simple cyanogen substitution products analogous to chloroacetic and the two chloropropionic acids. They are made by treating the chlorine products with potassium cyanide. They have been useful chiefly in the preparation of dibasic acids, as described in connection with malonic and the two succinic acids. It will therefore not be necessary to treat of them individually here.

NOTE FOR STUDENT. — How can malonic acid be made from acetic acid; and isosuccinic acid from propionic acid? Give the equations.

The chief substances to be taken up under the head of *mixed compounds containing nitrogen* are the amino acids and the acid amides. As will be seen, both these classes of substances are of special interest, as they represent forms of combination which are favorite ones in nature, especially in the animal kingdom, some of the most important substances found in the animal body, such as urea, uric acid, glycocoll, proteins, etc., belonging to one or both the classes.

### AMINO ACIDS

The relation of an amino acid to the simple acid is, as the name implies, the same as that of an amino derivative of a hydrocarbon to the hydrocarbon. That is to say, it is to be regarded as the acid in which the amino group,  $\text{NH}_2$ , has been substituted for a hydrogen atom of the hydrocarbon residue. Thus, aminoacetic acid is represented by the formula  $\text{H}_2\text{NCH}_2\text{COOH}$ ; while aminomethane, or methylamine, is represented thus,  $\text{CH}_3\text{NH}_2$ . The reasons for regarding methylamine as a substituted

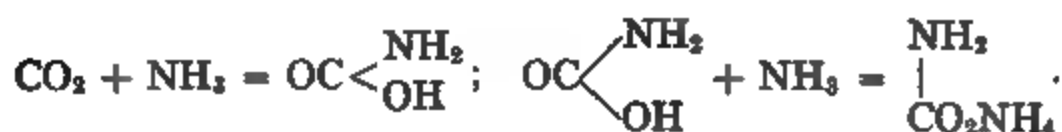
ammonia have been stated. The formula is based upon the reactions of the substance and the methods used in its preparation. The same arguments lead in the same way to the view that the amino acids are substituted ammonias, and, at the same time, acids. The simplest method for their preparation consists in treating halogen derivatives of the acids with ammonia. Thus aminoacetic acid can be made by treating bromoacetic acid with ammonia: —



NOTE FOR STUDENT. — Compare this reaction with that made use of for making methylamine.



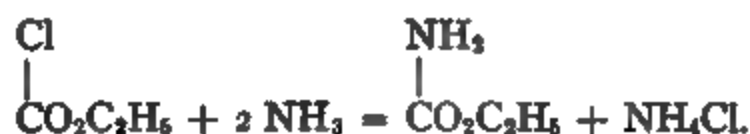
Aminoformic acid, carbamic acid,  $\text{H}_2\text{N}.\text{COOH}$ . — This acid is not known in the free condition. Its ammonium salt,  $\text{H}_2\text{N}.\text{CO}_2\text{NH}_4$ , is formed when dry carbon dioxide and dry ammonia are brought together, and it is therefore contained in commercial ammonium carbonate: —



The other carbamates are prepared from the ammonium salt. They are hydrolyzed when heated in aqueous solution, yielding carbonates and ammonia. Thus, when potassium carbamate is warmed in water solution, hydrolysis takes place, as represented in the equation: —



The *ethereal salts* of carbamic acid, called *urethanes*, are readily made by treating the ethereal salts of chlorocarbonic acid (178) with ammonia: —



Aminoformic acid cannot be taken as a fair representative of the amino acids, any more than carbonic acid can be taken as a fair representative of the hydroxy acids.

Glycocol, glycine, } (aminoethane acid)  $\left( \text{CH}_2 < \begin{smallmatrix} \text{NH}_2 \\ \text{CO}_2\text{H} \end{smallmatrix} \right)$ . —  
aminoacetic acid, }

In the bile there are two complicated acids, which are known as glycocholic and taurocholic acids. When glycocholic acid is boiled with hydrochloric acid, it breaks down, yielding cholic acid and glycocol. In the urine of horses is found an acid known as hippuric acid. When this is boiled with hydrochloric acid, it breaks down into benzoic acid and glycocol.

When uric acid is treated with hydriodic acid, glycocol is one of the products. Further, glycocol is formed when gelatin or glue is boiled with baryta water or dilute sulphuric acid. Its formation from bromoacetic acid and ammonia, mentioned above, gives the clearest indication in regard to its relation to acetic acid.

Aminoacetic acid is soluble in water, insoluble in absolute alcohol or ether. It has a sweetish taste, and is sometimes called *gelatin sugar*.

Aminoacetic acid has both acid and basic properties. It unites with strong acids, forming salts; and it combines with bases, giving metallic salts — the aminoacetates. The aminoacetates also unite with salts, forming double compounds.

Examples of the compounds with acids are the

*Hydrochloride* . . . . .  $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2.\text{HCl} \\ \text{CO}_2\text{H} \end{smallmatrix}$ ,

and the *Nitrate* . . . . .  $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2.\text{HNO}_3 \\ \text{CO}_2\text{H} \end{smallmatrix}$ ;

of the salts with metals,

*Zinc aminoacetate* . . . .  $\text{Zn}(\text{C}_2\text{H}_4\text{NO}_2)_2 + \text{H}_2\text{O}$ ,  
and *Copper aminoacetate* . .  $\text{Cu}(\text{C}_2\text{H}_4\text{NO}_2)_2 + \text{H}_2\text{O}$ ;

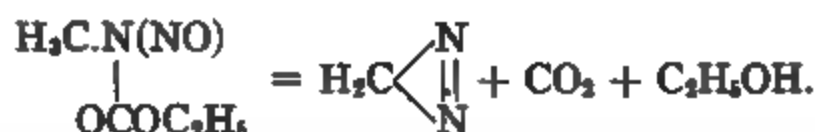
of the compounds with salts, the double salt of

*Copper nitrate* and  
*Copper aminoacetate* }  $\text{Cu}(\text{NO}_3)_2.\text{Cu}(\text{C}_2\text{H}_4\text{NO}_2)_2 + 2 \text{H}_2\text{O}$ .

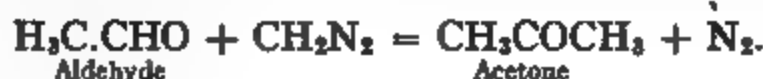


It was this decomposition which led to the discovery of hydrazine, and from this hydronitric or hydrazoic acid,  $\text{HN}_3$ .

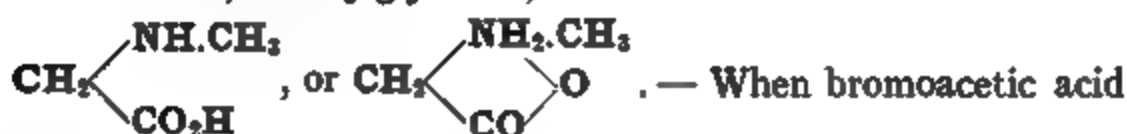
**Diazomethane**,  $\text{H}_2\text{C} \begin{smallmatrix} \nearrow \text{N} \\ || \\ \searrow \text{N} \end{smallmatrix}$ , is prepared by decomposing nitrosomethylurethane,  $\text{H}_3\text{CN}(\text{NO})\text{CO}_2\text{C}_2\text{H}_5$ , with a solution of an alkali:—



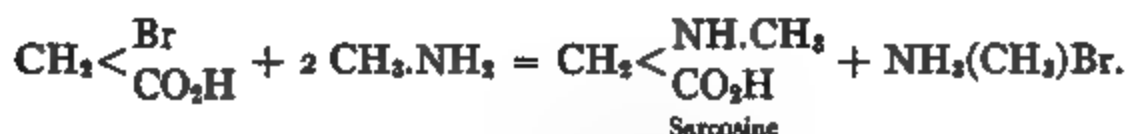
It is a yellow gas, exceedingly poisonous, and characterized by its remarkable chemical activity. It converts acids into methyl esters; alcohols (and phenols) into methyl ethers; primary amines into secondary amines (aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , into monomethylaniline,  $\text{C}_6\text{H}_5\text{NHCH}_3$ ), and aldehydes into ketones:



**Sarcosine**, methylglycocoll,



is treated with methylamine, a reaction takes place similar to that which takes place with ammonia, the product being *methylglycocoll* or *sarcosine*:—



Sarcosine is a product of the hydrolysis of creatine, which is found in flesh, and of caffeine, which is a constituent of coffee and tea. It is obtained from creatine and caffeine by boiling them with baryta water. Its properties are much like those of glycocoll. It is an inner ammonium salt.

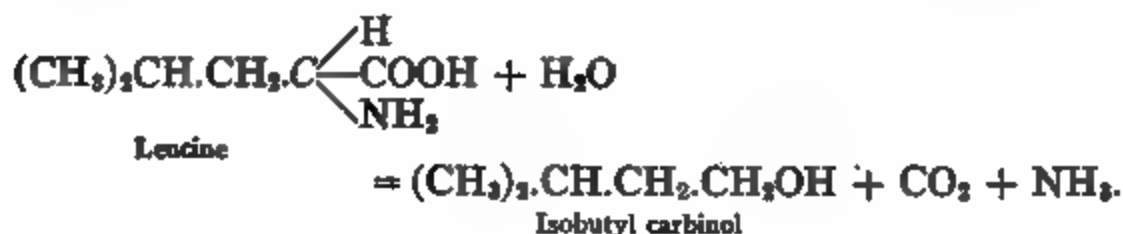
**Betaine**, trimethylglycine,  $\text{H}_2\text{C} \begin{smallmatrix} \nearrow \text{N}(\text{CH}_3)_3 \\ \searrow \text{CO} \end{smallmatrix} \text{O}$ , has been made synthetically from trimethylamine and monochloroacetic acid:—





When this inactive acid is resolved into its optically active components, the levo variety is found to be identical with the leucine obtained from natural sources.

When sugar is fermented with pure yeast in the presence of leucine, isobutyl carbinol (inactive isoamyl alcohol) is formed : —



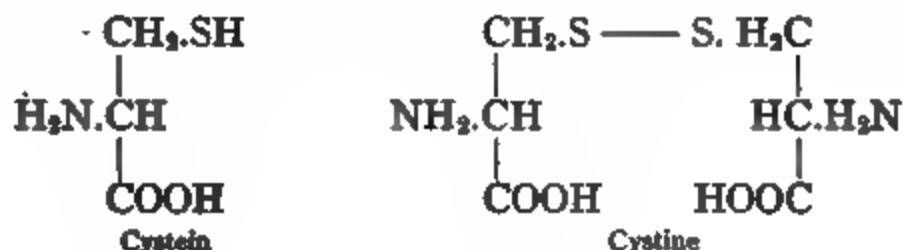
**Isoleucine, *d*-α-amino-β-methyl-β-ethyl propionic acid,**

$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3) > \text{CH}(\text{NH}_2).\text{COOH}$ , like leucine, is a frequent product of hydrolysis of vegetable and animal proteins. It is dextrorotatory and contains two asymmetric carbon atoms.

Isoleucine gives secondary butyl carbinol (active amyl alcohol) when fermented with sugar by pure yeast. (Write the equation.) Inactive amyl alcohol and active amyl alcohol (137) are the main constituents of fusel oil and result from the protein material contained in the potatoes or corn used in making alcohol.

**Serine**, which is obtained from silk glue by boiling with dilute acids, has been shown to be α-amino-β-hydroxypropionic acid,  $\text{CH}_2(\text{OH}).\text{CH}(\text{NH}_2).\text{COOH}$ , by treating it with nitrous acid when it gives glyceric acid (189). Optically active modifications are also known. It is formed in the hydrolysis of all albumins.

**Cystine**,  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$ , a substance sometimes found as a crystalline sediment in the urine of human beings and dogs, is a derivative of α-aminopropionic acid. It is frequently formed in the hydrolysis of proteins. Tin and hydrochloric acid reduce it to *cystein*,  $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ . The two substances bear to each other the relation represented by these formulas : —



## AMINOSULPHONIC ACIDS

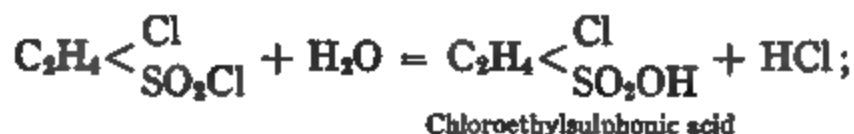
Just as there are amino derivatives of the carboxylic acids, so, too, there are amino derivatives of the sulphonic acids. The most important of these is



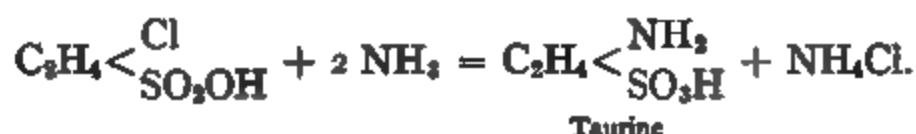
is found in combination with cholic acid as taurocholic acid, in ox bile, and the bile of many animals, as well as in the kidneys, lungs, etc. It has been made synthetically from isethionic acid (187) by first treating the acid with phosphorus pentachloride:—



The chloroethylsulphonyl chloride is then treated with water:—



and the chloroethylsulphonic acid with ammonia:—



Taurine crystallizes in large monoclinic prisms. It is a very stable substance, and can be boiled with concentrated acids without decomposition. With nitrous acid it yields isethionic acid.

It unites with strong bases forming salts, but not with acids. This is in accordance with the view that taurine is an inner

ammonium salt as represented by the formula  $\begin{array}{c} \text{CH}_2\text{—NH}_2 \\ | \\ \text{CH}_2\text{—SO}_2 \end{array} \text{O}.$

## AMINO DIBASIC ACIDS

Aspartic acid, aminosuccinic acid, aminobutane diacid,



Aspartic acid occurs in pumpkin seeds, and is frequently met with as a product of boiling various proteins with dilute acids. Thus, for example, it is formed when casein and albumin are treated in this way. It is formed also when asparagine (259) is boiled with acids or alkalies.

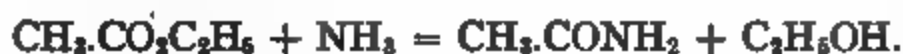
Aspartic acid crystallizes in rhombic prisms, which are difficultly soluble in water. The boiling solution of the natural product is levorotatory. A cold solution is dextrorotatory. It contains an asymmetric carbon atom, and the three varieties (*d*-, *l*-, and *dl*-) suggested by the theory are known. When treated with nitrous acid, each is converted into the corresponding malic acid.

### ACID AMIDES

When the ammonium salt of acetic acid is heated, it gives off water, and a compound distills over which is known as *acetamide*, *ethane amide*. The reaction is represented by the following equation:—



An investigation of the ammonium salts of other carboxylic acids shows that the reaction is a general one, and a class of compounds, known as the *acid amides*, can thus be obtained. Besides this method there are two others of general application for the preparation of the acid amides. One consists in treating an ethereal salt of an acid with ammonia. Thus, when ethyl acetate is treated with ammonia, this reaction takes place:—



The other reaction consists in treating the acid chlorides with ammonia. Thus, to get acetamide, we may treat acetyl chloride (60) with ammonia:—



This last reaction is perhaps most frequently used. It shows the relation that exists between acetic acid and acetamide.

For acetyl chloride is made from acetic acid by treatment with phosphorus trichloride, and is, therefore, to be regarded as acetic acid in which the hydroxyl is replaced by chlorine. Now, by treatment with ammonia the same reaction takes place as that which we have had to deal with in the preparation of amino acids; the chlorine is replaced by the amino group. Therefore, acetamide is acetic acid in which the hydroxyl is replaced by the amino group, as shown in the formulas:—



As the hydroxyl of the acid is replaced, the amide is not an acid. On the other hand, the basic properties of the amino group are weakened by the presence of the acid residue as a part of its composition. Acetamide combines with hydrochloric acid gas, and the hydrogen atoms of the amino group can be replaced by metals, owing to the acidifying influence of the CO-group. It is therefore a weak base and at the same time a weak acid.

The amides are converted into ammonia and a salt of the acid when boiled with solutions of strong bases:—



They are converted into cyanides by distilling with phosphorus pentoxide,  $\text{P}_2\text{O}_5$ :—



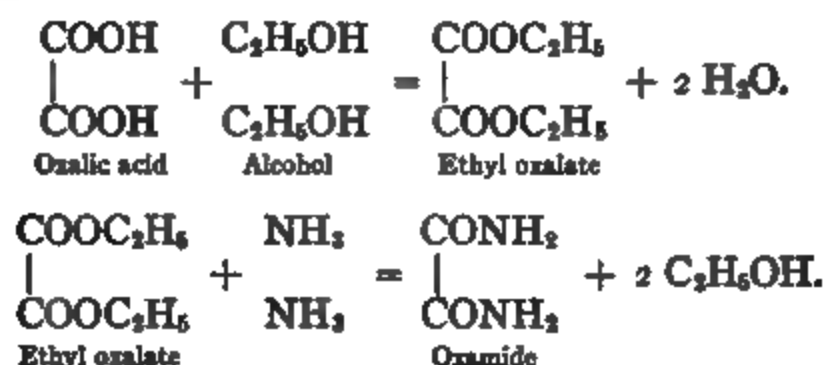
As the substance obtained in this way is identical with methyl cyanide, which is formed by heating the potassium salt of methylsulphuric acid with potassium cyanide, the reaction furnishes additional evidence in favor of the conclusion that in the cyanides the carbon and not the nitrogen of the cyanogen group is in combination with the hydrocarbon residue, as represented in the formula  $\text{CH}_3-\text{C}\equiv\text{N}$ .

As the amide can be made from the ammonium salt, and the cyanide or nitrile from the amide, so, by starting with the cyanide, the amide and the ammonium salt can be made. The reaction by which the cyanides are converted into acids is based upon these relations:—

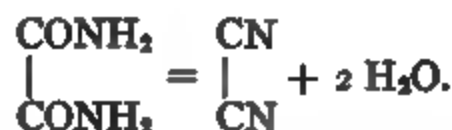


By treating acid amides with acid chlorides, more complicated compounds can be obtained. Of these *diacetamide*,  $\text{NH}(\text{C}_2\text{H}_3\text{O})_2$ , and *triacetamide*,  $\text{N}(\text{C}_2\text{H}_3\text{O})_3$ , may serve as examples.

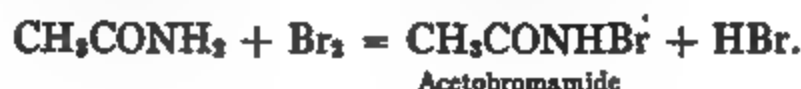
The preparation of an acid amide by treating an ester with ammonia is well illustrated by the preparation of oxamide, in which ethyl oxalate is first prepared and this then converted into the amide by treating it with aqueous ammonia:—



When oxamide is heated with a dehydrating agent, such as phosphorus pentoxide, it is converted into cyanogen:—



**Hofmann's reaction.**—When an acid amide is treated with bromine in an excess of sodium hydroxide, the first product formed is acetobromamide,  $\text{CH}_3\text{CONHBr}$ :—

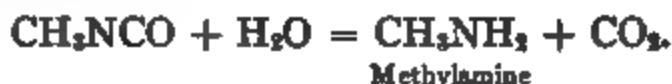


The sodium hydroxide reacts with the bromamide (which has acid properties owing to the presence of the carbonyl group and

the bromine atom) to form a salt,  $\text{CH}_3\text{CONa.NBr}$ , which is unstable. This sodium bromamide undergoes molecular rearrangement (compare with the Beckmann rearrangement, 401): —



and the intermediate product by the loss of sodium bromide forms methyl isocyanate. This, in the presence of the alkali, gives the primary amine and carbon dioxide: —

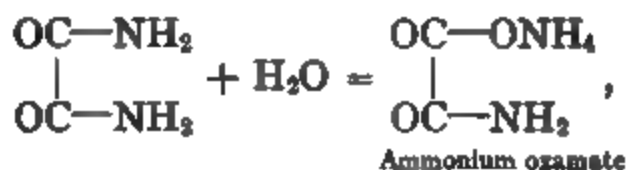


It is thus possible by starting with any acid to pass to the primary amine containing the same hydrocarbon radical as the acid. In the case of acetic acid the three stages are represented below: —



This reaction has become of practical importance in connection with the preparation of anthranilic acid (407).

**Amic acids.** — When the amide of a dibasic acid (as oxamide) is boiled with aqueous ammonia hydrolysis takes place: —



and the ammonium salt of oxamic acid,  $\text{HOOC.CONH}_2$ , results. Oxamic acid, like carbamic acid (248), is both an acid and an amide. It forms salts and other derivatives characteristic of acids, and, like the amides of the acids, is hydrolyzed by alkalies or acids to oxalic acid and ammonia.

There is one acid of this kind that is a well-known natural substance. It has already been referred to in connection with aspartic acid, which is closely related to it. It is

**Asparagine, aminosuccinamic acid,  $C_4H_7N_2O_3 + H_2O$ ,  $CH_2.CONH_2$**   
 $\begin{array}{c} | \\ CH(NH_2).COOH \end{array}$ . — Asparagine is found in many plants, as in

asparagus, beets, peas, beans, vetches, and in wheat. It can be made by treating monoethyl aminosuccinate with ammonia.

**NOTE FOR STUDENT.** — What reaction takes place? Write the equation. How is monoethyl aminosuccinate made?

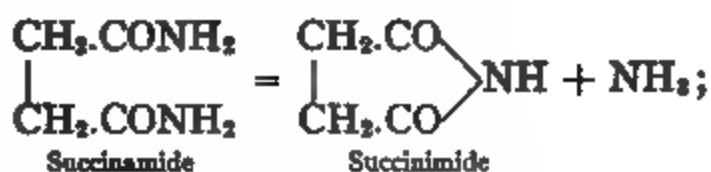
Asparagine forms large rhombic crystals, difficultly soluble in cold water, more easily in hot water. When boiled with acids or alkalies, it is converted into aspartic acid and ammonia.

**NOTE FOR STUDENT.** — Note that only the amino group of the amide is driven out of the compound by this treatment. The other amino group which is contained in the hydrocarbon portion of the compound is not affected.

Nitrous acid converts the asparagines into the malic acids.

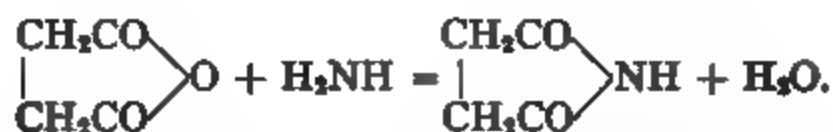
Asparagine contains an asymmetric carbon atom, and two optically active stereoisomeric varieties are known. The levorotatory variety is found in the seeds of many plants, in asparagus, in beets, in peas, beans, and in vetch sprouts. The dextro variety is also found in vetch sprouts. It is distinguished from ordinary asparagine by its sweet taste.

**Succinimide,  $C_4H_5NO$** . — This compound deserves attention in this connection, as it represents a not uncommon class known as the *acid imides*. They are formed from polybasic acids, most simply from dibasic acids. They may be regarded as the anhydrides in which the imino group has been substituted for an oxygen atom. They are formed from the amides by loss of ammonia. Thus: —



and from the anhydrides by the action of ammonia: —

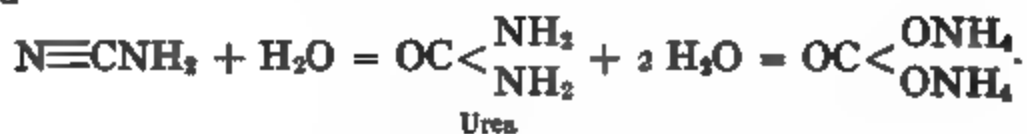
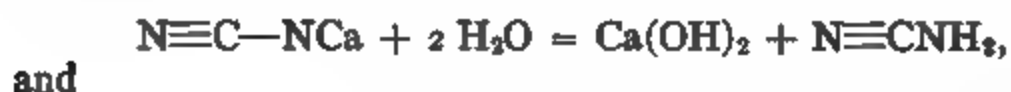




The hydrogen atom of the imido group is replaceable by some metals, or the imide has the properties of a weak acid.

**Cyanamide,  $\text{N}\equiv\text{C}-\text{NH}_2$ .** — In treating of cyanic acid, the existence of two chlorides of cyanogen was mentioned: one, a liquid having the formula  $\text{NCCl}$ ; the other, a solid of the formula  $\text{N}_3\text{C}_3\text{Cl}_3$ . When the former is treated with ammonia, it is converted into an amide,  $\text{NC.NH}_2$ , which bears to cyanic acid,  $\text{NC.OH}$ , the relation of an amide. Like the other simple compounds of cyanogen, cyanamide readily undergoes change. Heated to  $150^\circ$  or when allowed to stand, it is converted into *dicyandiamide*,  $\text{C}_2\text{N}_4\text{H}_4$ ; while, when heated to above  $150^\circ$ , a violent reaction takes place, and *tricyantriamide*,  $\text{C}_3\text{N}_6\text{H}_6$ , is formed. The latter compound is also called *melamine* and *cyanuramide*, and from certain methods of formation it is concluded that it is the amide of cyanuric acid. It is a strong monacid base. The formation of these compounds is particularly interesting, as illustrating the tendency on the part of the simple cyanogen compounds to undergo polymerization.

**Calcium cyanamide,  $\text{N}\equiv\text{C}-\text{NCa}$ .** — This compound has come into prominence as a fertilizer. In the soil it furnishes the nitrogen necessary for the growth of plants: —



It is made by passing nitrogen over calcium carbide heated to  $750^\circ$ – $1000^\circ$  in an electric furnace, when the reaction represented in this equation takes place: —



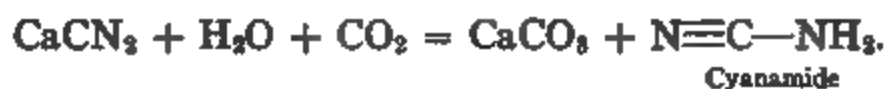
The nitrogen used is obtained by fractional distillation of liquid air. The absorption of nitrogen is increased by the presence of 10 per cent calcium chloride.

Calcium cyanamide when treated with superheated steam gives off all its nitrogen in the form of ammonia:—

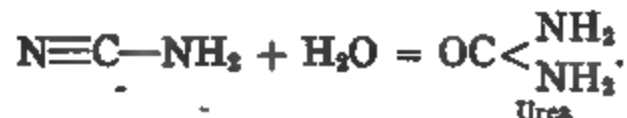


This is one of the methods of "fixing" the nitrogen of the air. The ammonia obtained by this method is very pure and may be used in making ammonium salts or it may be converted by catalytic oxidation into nitric acid, thus converting the nitrogen of the air into the valuable nitric acid now obtained from Chili saltpeter.

When calcium cyanamide in water is treated in the cold with carbon dioxide, calcium carbonate is precipitated and a solution of pure cyanamide is obtained:—



By heating this solution, in the presence of a catalyst, such as manganese superoxide, the cyanamide takes up water, forming urea:—



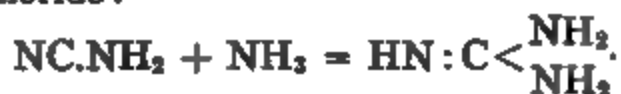
This is a technical method for the manufacture of urea on the large scale. It is a synthesis of urea from coal, nitrogen of the air and water, that is, from the elements.

About 180,000 tons of calcium cyanamide are produced annually.

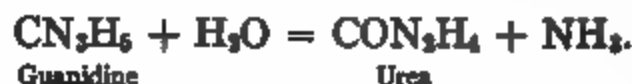
**Guanidine,  $\text{CN}_3\text{H}_5$ .**—This substance, which is closely related to cyanamide, was first obtained by the oxidation of guanine (271). It can also be made by treating cyanogen iodide with ammonia:—



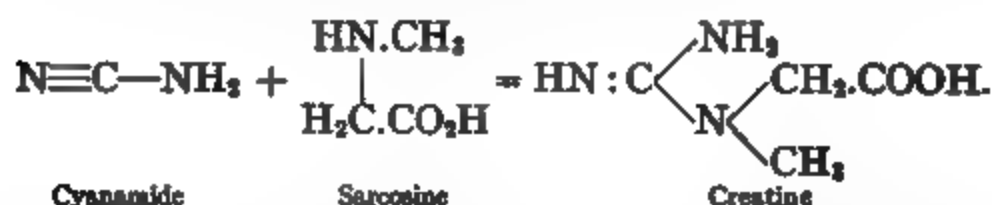
the product being the hydriodic acid salt of guanidine. It is best made by heating the alcoholic solution of cyanamide with ammonium chloride:—



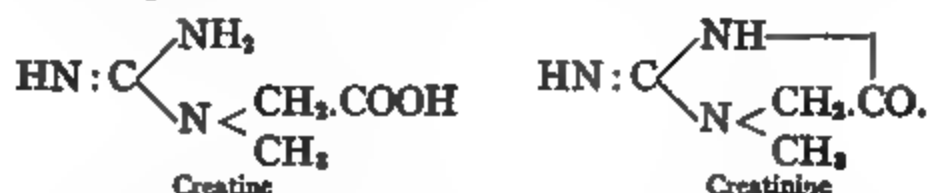
It is a very strong alkaline base. Boiled with dilute sulphuric acid or baryta water, it yields urea and ammonia: —



**Creatine,  $\text{C}_4\text{H}_7\text{N}_3\text{O}_2$ .** — This substance is found in the muscles of all animals. It is usually made from "extract of meat." It has been made synthetically by bringing cyanamide and sarcosine together. The reaction is analogous to that made use of for the preparation of guanidine: —



**Creatinine,  $\text{C}_4\text{H}_7\text{N}_3\text{O}$ ,** in small quantity is a constant constituent of human urine. Creatine is converted into creatinine by the loss of water when its solution is heated with dilute hydrochloric acid. In contact with alkalies creatinine gradually takes up the elements of water and forms creatine. It is a base, forming with acids well-crystallized salts. Its relation to creatine is represented thus: —



**Urea, carbamide, and derivatives.** — Closely related to the nitrogen compounds just referred to is urea, or the amide of carbonic acid. Its importance and certain reactions distinguish it from the other acid amides, and it is therefore treated by itself.

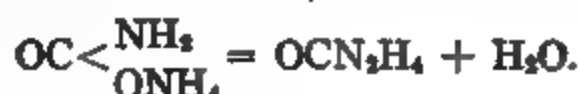
Urea is found in the urine and blood of all mammals, and particularly in the urine of carnivorous animals. It is the final decomposition product of the proteins in the animal body. Human urine contains from 2 to 3 per cent; the quantity given off by an adult man in 24 hours being about 30 grams. Urea can be made by the following methods: —

(1) By treating carbonyl chloride with ammonia:—

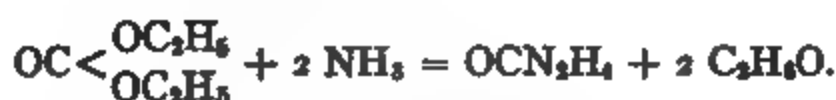


(What is the analogous reaction for the preparation of acetamide?)

(2) By heating ammonium carbamate:—



(3) By treating ethyl carbonate with ammonia:—



(4) By the addition of water to cyanamide:—



(5) By evaporation of ammonium cyanate in aqueous solution:—



This reaction is of special interest, for the reason that it was the first example of the formation, by artificial methods from inorganic substances, of an organic compound found in the animal body (1).

Urea is readily obtained from urine. It crystallizes from alcohol in large, rhombic prisms, which melt at  $132^\circ$ . It is easily soluble in water and alcohol. Heated with water in a sealed tube to  $180^\circ$ , or boiled with dilute acids or alkalis, it breaks down into carbon dioxide and ammonia:—



The same decomposition of urea takes place when urine is allowed to stand. Hence the odor of ammonia is always noticed in the neighborhood of stables and urinals that are not kept thoroughly clean. This decomposition is due to the action of a microorganism known as *micrococcus ureæ*. This change is a good example of the way in which nature converts useless material into useful ones. Urea is a waste-product of the life-process.

After it has left the body it ceases to be of value, whereas carbon dioxide and ammonia are essential to the life of plants.

The enzyme, *urease*, present in the extract of soy bean, hydrolyzes urea into ammonium carbonate, and this affords one of the best methods of estimating urea.

Sodium hypochlorite or hypobromite decomposes urea into carbon dioxide, nitrogen, and water:—

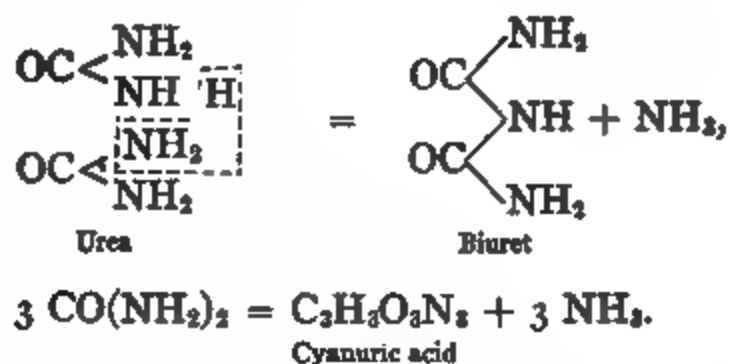


The carbon dioxide is absorbed by the solution which contains sodium hydroxide, and the nitrogen can then be measured. From the volume of nitrogen obtained the amount of urea can be calculated. This is the basis of one of the methods used for estimating urea.

Nitrous acid acts in a similar way:—



When heated, urea loses ammonia, and yields, first, *biuret* and, finally, *cyanuric acid* (90):—



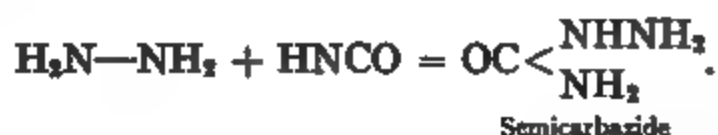
Biuret in alkaline solution gives a beautiful violet to red color with a drop or two of 2 per cent solution of copper sulphate. This biuret reaction is characteristic of the proteins and some of the more complicated polypeptides (271).

Urea unites with acids, bases, and salts. The hydrogen of the amino groups can be replaced by acid or alcohol radicals, giving compounds of which *acetyl urea*,  $\text{OC} \begin{array}{l} \text{NH.C}_2\text{H}_5\text{O} \\ \text{NH}_2 \end{array}$ , and *ethylurea*,  $\text{OC} \begin{array}{l} \text{NHC}_2\text{H}_5 \\ \text{NH}_2 \end{array}$ , are examples.

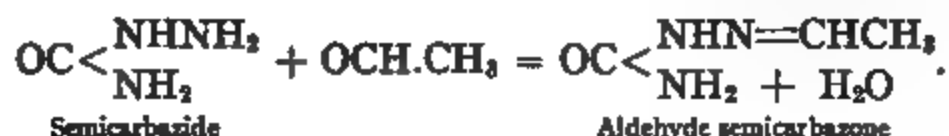
Among the compounds with acids, the following may be mentioned: *urea hydrochloride*,  $\text{CH}_4\text{N}_2\text{O} \cdot \text{HCl}$ ; *urea nitrate*,  $\text{CH}_4\text{N}_2\text{O} \cdot \text{HNO}_3$ ; and *urea phosphate*,  $\text{CH}_4\text{N}_2\text{O} \cdot \text{H}_3\text{PO}_4$ . With *mercuric oxide*,  $2 \text{HgO} \cdot \text{CH}_4\text{N}_2\text{O}$ ; with *silver*,  $\text{CH}_2\text{N}_2\text{O} \cdot \text{Ag}_2$ , etc. With salts it forms such compounds as  $2 \text{CO}(\text{NH}_2)_2 \cdot \text{Hg}(\text{NO}_3)_2 \cdot 3 \text{HgO}$ , etc.

Urea is used as a stabilizer in smokeless powders and celluloid, and in the preparation of medical remedies (veronal, etc.).

**Semicarbazide,  $\text{H}_2\text{NCONH.NH}_2$ .**—Hydrazine hydrate unites with potassium cyanate to form *semicarbazide*:—



This is an *amino derivative of urea*. Like hydroxylamine and phenylhydrazine it reacts with aldehydes and ketones : —

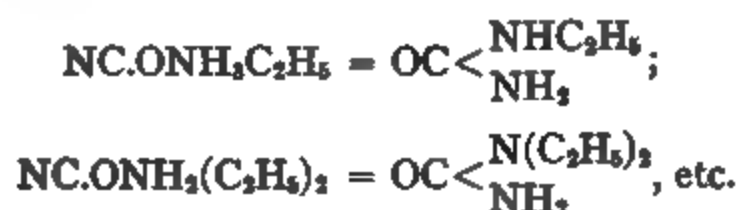


As the semicarbazones are well crystallized compounds with sharp melting points, semicarbazide is frequently used as a reagent for aldehydes and ketones.

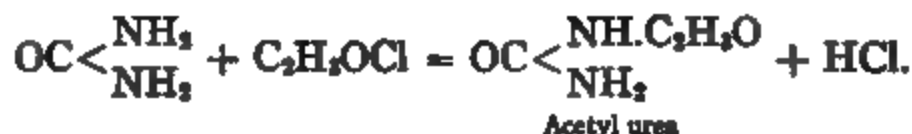
**Substituted ureas.**—These are derivatives of urea which contain hydrocarbon residues in place of one or all the hydrogen atoms. They can be made from the cyanates of substituted ammonias. The fundamental reaction is the spontaneous transformation of ammonium cyanate into urea:—



In the same way, cyanates of substituted ammonias are transformed into substituted ureas: —

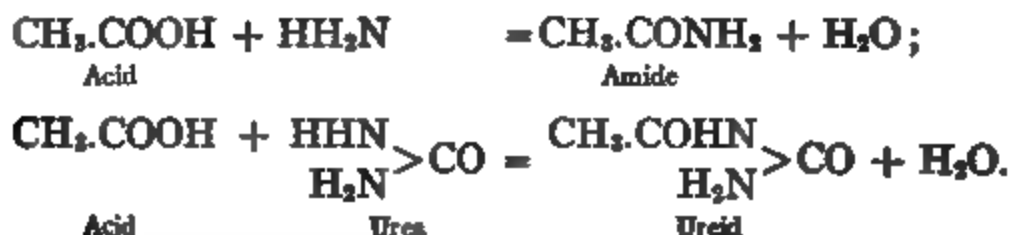


The urea derivatives which contain acid radicals are made by treating urea with the acid chlorides:—

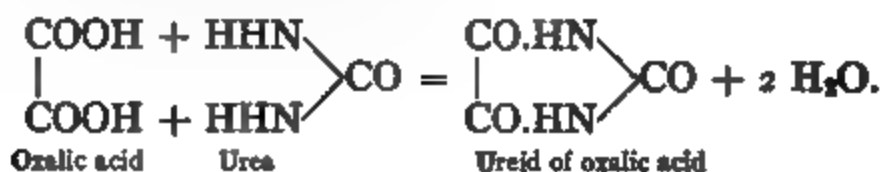


NOTE FOR STUDENT. — In what sense is acetyl urea analogous to acetamide?

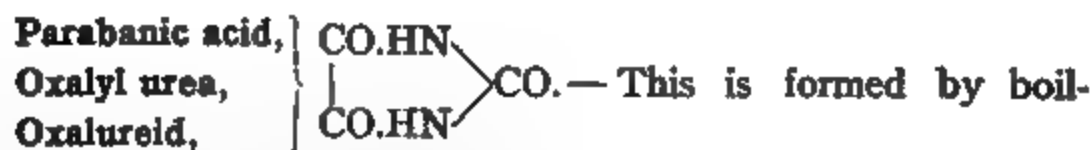
Ureids are compounds derived from urea by the substitution of acid residues for one or more of the hydrogen atoms. Thus, acetyl urea is a simple ureid. The relation between the ureid and the amide is shown in the equations:—



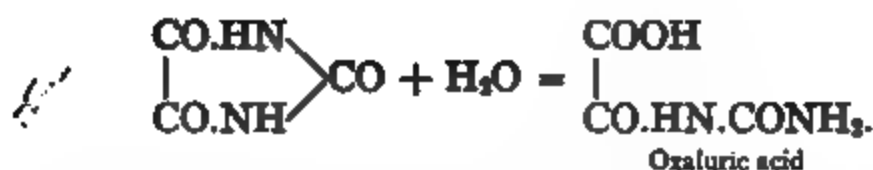
The ureids of dibasic acids resemble in the same way the imides of these acids. One urea residue takes the place of the two acid hydroxyls. Thus, in the case of oxalic acid the relation is shown by the formulas below:—



There are several compounds of this kind that are of importance:—



ing uric acid with strong nitric acid and with other oxidizing agents, and by treating a mixture of oxalic acid and urea with phosphorus oxychloride. It acts like an acid, the hydrogen of the imido group being replaceable by metals, as in succinimide. It readily passes over into salts of oxaluric acid when heated with a solution of an alkali:—



Oxaluric acid bears to parabanic acid the same relation that oxamic acid bears to oxamide. It occurs in the form of the ammonium salt in small quantity in human urine. With phosphorus oxychloride it gives parabanic acid by the loss of water.

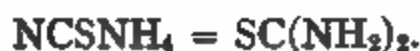
Barbituric acid, malonyl urea,  $\text{C}_4\text{H}_4\text{N}_2\text{O}_3 + 2 \text{H}_2\text{O}$ ,



is obtained from uric acid by the action of dilute nitric acid. It has been made artificially by treating a mixture of malonic acid and urea with phosphorus oxychloride. Heated with a solution of an alkali, it breaks down into malonic acid and urea.

Diethylbarbituric acid,  $\text{C}(\text{C}_2\text{H}_5)_2 \langle \begin{array}{c} \text{CO.NH} \\ \text{CO.NH} \end{array} \rangle \text{CO}$ , made by the action of the diethyl ester of diethylmalonic acid upon urea, *fulum* is an excellent soporific. It is known as *veronal*. The monosodium salt, which is soluble in water, is known as *medinal*, and is also a soporific.

Thiourea,  $\text{SC}(\text{NH}_2)_2$ . — This substance is formed by fusing ammonium thiocyanate, the reaction being analogous to that by which urea is formed from ammonium cyanate: —



It forms rhombic prisms melting at  $172^\circ$ . It combines with one equivalent of acids, forming salts.

A number of derivatives of thiourea have been made. They resemble those obtained from urea.

Uric acid,  $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ . — Uric acid occurs in human urine in small quantity, in the urine of carnivorous animals, and in the excrement of birds and of reptiles. In these animals this substance takes the place of urea, and most of the nitrogen excretion is in this form. The excrement of reptiles consists

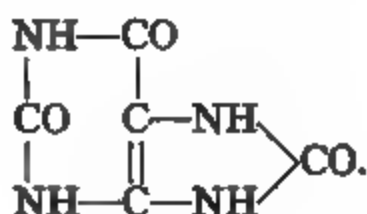


almost wholly of ammonium urate. In arthritis and gout, uric acid is deposited in the joints, in the form of insoluble acid salts. It also occurs frequently in this form in urinary sediment and sometimes in the bladder as calculi.

Uric acid forms colorless, crystalline scales, and is almost insoluble in water. It acts like a weak dibasic acid.

When an aqueous solution of uric acid in alkali is shaken with methyl iodide, tetramethyluric acid,  $C_5(CH_3)_4N_4O_3$ , is formed. When this is hydrolyzed with concentrated hydrochloric acid, all the nitrogen is given off in the form of *methylamine*; no ammonia is formed. This proves that in tetramethyluric acid the four nitrogen atoms are all combined with methyl, and hence that in uric acid the four hydrogen atoms are present in the form of imino groups,  $C_5(NH)_4O_3$ .

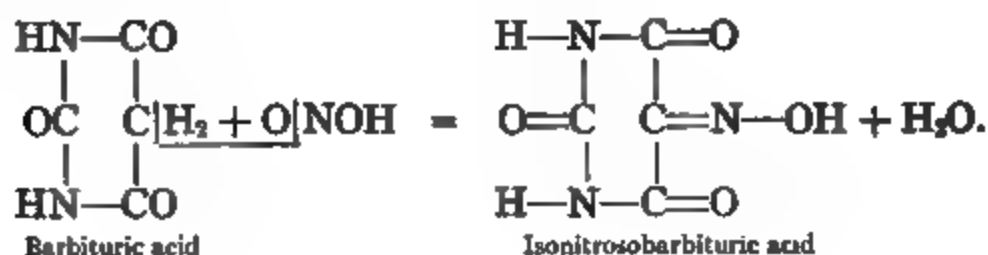
Other transformations show that the constitution of the acid must be represented by the formula



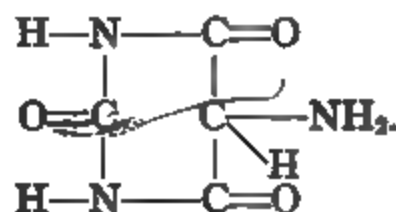
According to this, uric acid contains two urea residues combined in different ways with the group  $\begin{array}{c} \text{CO} \\ | \\ \text{C} \\ || \\ \text{C} \end{array}$ . It is to be re-

garded as a diureid of a hypothetical trihydroxyacrylic acid,  $(\text{HO})_2\text{C}=\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ . That this view is correct has been shown by the following synthesis of uric acid:—

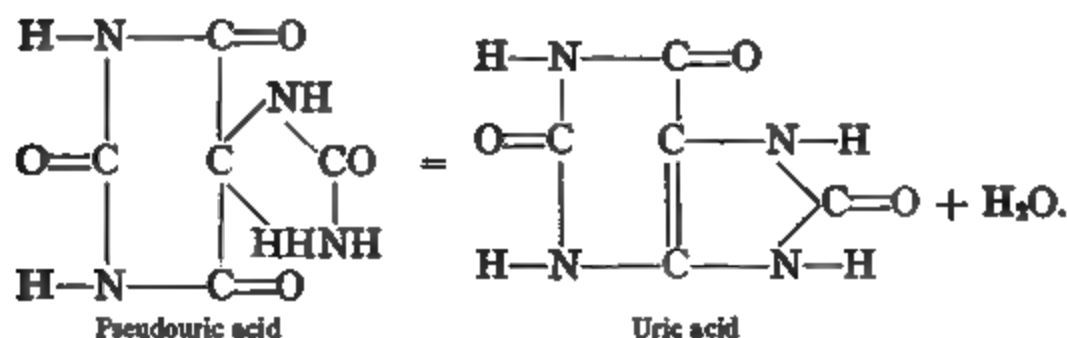
Barbituric acid with nitrous acid gives the isonitroso compound:—



By reduction this forms aminobarbituric acid,

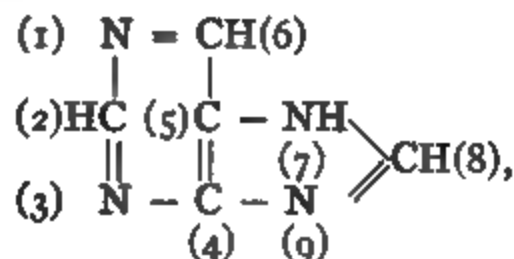


This combines with potassium cyanate, forming a potassium salt of pseudouric acid (analogous to the formation of semi-carbazide). This acid loses a molecule of water and gives uric acid as shown below.



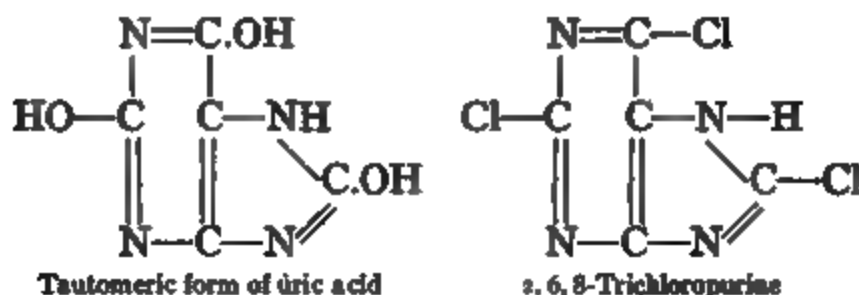
It will be seen that uric acid contains residues not only of urea, but of parabanic acid, of barbituric acid, and of a ureid of mesoxalic acid (alloxan). All these ureids have been made from uric acid by the action of nitric acid.

Uric acid and related compounds are derived from a compound of the formula,



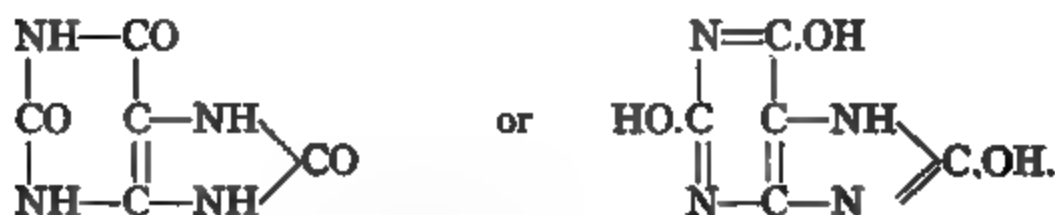
to which the name *purine* has been given.

Purine has been made from uric acid by first treating it with phosphorus oxychloride, which gives trichloropurine:—



On reduction this gives purine.

As shown above, uric acid acts as a tautomeric compound. It may be represented by either one of the two formulas,



According to the latter formula it is 2, 6, 8-trihydroxypurine.

**Xanthine**, 2, 6-dihydroxypurine,  $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$ , is found in all the tissues of the body and in the urine, in some rare urinary calculi, and in several animal liquids. It is formed by the action of nitrous acid on guanine: —



In this case the nitrous acid causes a substitution of a hydroxyl group for an amino group.

**Theobromine**,  
**3,7-Dimethylxanthine**, }  $\text{C}_7\text{H}_8(\text{CH}_3)_2\text{N}_4\text{O}_2$ , is a substance found in chocolate prepared from the seed of the cacao tree. It has been made by treating the lead salt of xanthine with methyl iodide.

**Theophylline**, 1, 3-dimethylxanthine, is found in tea.

**Caffeine**, theine, 1, 3, 7-trimethylxanthine,



is the active constituent of coffee and tea. It has been made from theobromine and from theophylline by the introduction of a third methyl group.

Thus, as will be seen, a close connection is established between the active constituents of coffee, tea, and chocolate on the one hand, and xanthine and guanine on the other.

✓ Guanine, 2-amino-6-hydroxypurine,  $C_5H_4(NH_2)N_4O$ , is found principally in guano, from which it is prepared. Oxidizing agents convert it into guanidine,  $CN_3H_5$ . Nitrous acid converts it into xanthine. It is a remarkable fact that amino compounds are readily transformed into hydroxy compounds in the animal organism by means of enzymes; e.g., guanase, found in the liver, spleen, lungs, etc., hydrolyzes guanine, forming xanthine and ammonia.

Polypeptides are compounds, closely related to the proteins (538), which have been made from the amino acids. The simplest example is *glycylglycine*,  $(H_2N.CH_2.CO).NH.CH_2.COOH$ , a derivative of glycine,  $H_2N.CH_2.COOH$ , in which one of the amino hydrogens is replaced by the glycy group,  $NH_2.CH_2.CO$ . It is called a *dipeptide*, as it contains *two* residues of an amino acid. The simplest method of making it is to treat glycine with chloroacetyl chloride (made from chloroacetic acid):—



The chloroacetylglycine formed is then treated with ammonia:—



Glycylglycine reacts in the same way with chloroacetyl chloride, giving chloroacetylglycylglycine,



which reacts with ammonia to give the tripeptide,



In a similar manner polypeptides containing 4, 5, 6, and as many as 18, residues of amino acids have been prepared by Emil

Fischer. This last polypeptide contains 15 glycine, and 3 leucine residues and has a molecular weight of 1213. It is one of the most complex substances of known structure that has ever been made synthetically.

The higher polypeptides resemble the peptones (541) very closely in their properties, indicating a similarity in their chemical structure. For example, most of them are soluble in water, insoluble in alcohol, and they have a bitter taste like the peptones. They are precipitated by phosphotungstic acid, give the biuret test (264), and are completely hydrolyzed to amino acids by boiling with hydrochloric acid, reactions which are characteristic of the proteins and the peptones. Some of the polypeptides have been found among the hydrolytic cleavage products of the proteins, and some of the synthetic polypeptides are hydrolyzed to amino acids by the enzyme, trypsin, of the pancreatic juice just as the peptones are. Pepsin, the enzyme found in the gastric juice, which hydrolyzes the proteins to peptones, does not hydrolyze the polypeptides. There is no doubt that peptones are complicated mixtures of polypeptides.

C. C. <sup>1213</sup>  
1213

## CHAPTER XIII

### UNSATURATED CARBON COMPOUNDS

**Distinction between Saturated and Unsaturated Compounds.**—Most of the compounds thus far studied are called *saturated compounds*. This is an appropriate name so far as the hydrocarbons themselves and some of the classes of their derivatives are concerned. The expression *saturated* is intended to signify that the compounds have no power to unite directly with other compounds or elements. Thus, marsh gas cannot be made to unite directly with anything. Bromine, for example, must first displace hydrogen before it can enter into combination:—



Therefore marsh gas is saturated.

On the other hand, a compound that can take up elements or other compounds directly is called *unsaturated*. Thus, phosphorus trichloride is unsaturated, for it has the power to take up two chlorine atoms:—



Ammonia is unsaturated, for it can take up a molecule of a monobasic acid:—



The condition of unsaturation is met with among carbon compounds in several forms:—

*First.* The aldehydes act like unsaturated compounds, as shown in their power to take up hydrogen, ammonia, hydrocyanic acid, sodium bisulphite, etc.

*Second.* The ketones also act like unsaturated compounds,

though their power in this respect is less marked than that of the aldehydes.

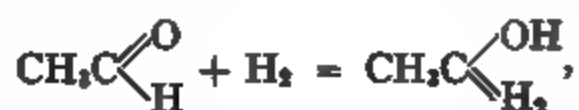
*Third.* The substituted ammonias are unsaturated, in the same sense that ammonia itself is unsaturated.

*Fourth.* The cyanides take up hydrogen directly, and are therefore unsaturated also.

In the cyanides carbon and nitrogen are linked together in a different way from that in the substituted ammonias, and when hydrogen is added to the cyanogen group,  $\text{—C:N}$ , the condition is changed to that which is characteristic of the substituted ammonias:—



In the aldehydes and ketones, carbon is in combination with oxygen in the carbonyl condition. When they unite with hydrogen and some compounds, such as hydrocyanic acid, the relation between the carbon and oxygen is changed to the hydroxyl condition. The changes are represented by formulas such as the following:—



*Fifth.* There is a fifth kind of unsaturation, *dependent upon differences in the relations between carbon atoms*, and it is this kind which is ordinarily meant when *unsaturated carbon compounds* are spoken of.

The kind of relation between the carbon atoms in all the saturated hydrocarbons is the same as that which exists between the two carbon atoms of ethane, and this is represented by the formula  $\text{H}_3\text{C—CH}_3$ . This formula signifies simply that the two carbon atoms are held together by the bonds which in marsh gas enabled each methyl group to hold one hydrogen atom. Abstracting *one hydrogen atom* from each of two molecules of marsh gas, union is effected between the carbon atoms. What

would result if *two hydrogen atoms* were abstracted, and union between the carbons then effected? Theoretically we should get a compound made up of two groups  $\text{CH}_2$ , thus  $\text{H}_2\text{C}:\text{CH}_2$ , and presumably the relation between the carbon atoms in this compound would be different from the relation between the carbon atoms in ethane. Without pushing these speculations farther, it may be said that there is a well-known hydrocarbon of the formula  $\text{C}_2\text{H}_4$  that differs markedly from ethane. It shows the property of unsaturation very clearly. This is *olefiant gas* or *ethylene*. It is the first of an homologous series of hydrocarbons, only a few of which are well known. These hydrocarbons yield derivatives like those obtained from the paraffins; though of these few are known as compared with the number of the paraffin derivatives.

UNSATURATED NORMAL HYDROCARBONS  $\text{C}_n\text{H}_{2n}$   
OLEFINES, ALKYLENES

FORMULA	NAME	MELTING POINT	BOILING POINT
$\text{C}_2\text{H}_4$	Ethylene, Ethene	$-169^\circ$	$-102.5^\circ$
$\text{C}_3\text{H}_6$	Propylene, Propene		$-47.8$
$\text{C}_4\text{H}_8$	Butylene, Butene		$1-1.5$
$\text{C}_5\text{H}_{10}$	Amylene, Pentene		$39.40$
$\text{C}_6\text{H}_{12}$	Hexylene, Hexene	$-98.5$	$67.7$
$\text{C}_7\text{H}_{14}$	Heptylene, Heptene		$98-99$
$\text{C}_8\text{H}_{16}$	Octylene, Octene		$124$
$\text{C}_9\text{H}_{18}$	Nonylene, Nonene		$147-148$
$\text{C}_{10}\text{H}_{20}$	Decylene, Docene		$172$
$\text{C}_{11}\text{H}_{22}$	Undecylene		$195.4$
$\text{C}_{12}\text{H}_{24}$	Dodecylene	$-31.5$	$213-215$
$\text{C}_{13}\text{H}_{26}$	Tridecylene		$232.7$
$\text{C}_{14}\text{H}_{28}$	Tetradecylene	$-12$	$127 (15, \text{mm})$
$\text{C}_{15}\text{H}_{30}$	Pentadecylene		$247$
$\text{C}_{16}\text{H}_{32}$	Hexadecylene	$4$	$274$
$\text{C}_{18}\text{H}_{36}$	Octadecylene	$18$	$179 (15, \text{mm})$
$\text{C}_{26}\text{H}_{52}$	Cerotene	$58$	—
$\text{C}_{28}\text{H}_{56}$	Melene	$62$	$370-380$

The members are homologous with ethylene. They bear to the paraffins a very simple relation, each one containing two atoms of hydrogen less than the paraffin with the same number of carbon atoms.



**Ethylene, ethene, olefiant gas,  $C_2H_4$ ,  $CH_2=CH_2$ .** — This gas is formed from many organic substances when they are subjected to dry distillation. The two principal reactions which yield it are : —

(1) The action of an alcoholic solution of potassium hydroxide on ethyl chloride, bromide, or iodide : —



This is the most important reaction for the preparation of the unsaturated compounds of the ethylene series. It is applicable not only to the hydrocarbons but to their derivatives. By means of it it is possible to pass from any saturated compound to the corresponding unsaturated compound of the ethylene series. Thus we can pass from ethane,  $C_2H_6$ , to ethylene,  $C_2H_4$ , by first introducing bromine, and then abstracting hydrobromic acid from the monobromine substitution product. By treating the monobromine substitution products of other saturated compounds in the same way, the corresponding unsaturated compounds can be made.

(2) The action of sulphuric acid and other dehydrating agents upon alcohol : —



In the case of sulphuric acid, ethyl acid sulphate is first formed. This when heated gives ethylene and sulphuric acid : —



Ethylene is made on the large scale by passing the vapor of ethyl alcohol over clay balls heated to  $300^\circ$  to  $400^\circ$  :

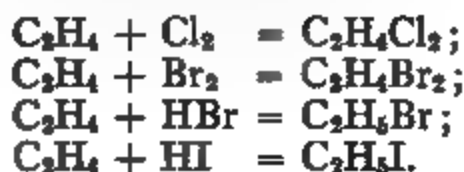


Ethylene is made most conveniently in the laboratory from ethylene bromide by removing the two bromine atoms by means of the zinc copper couple : —



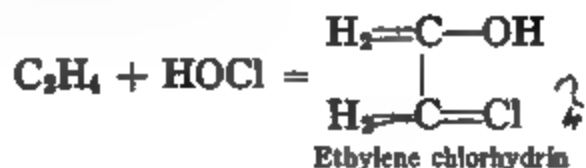
Ethylene is a colorless gas with a characteristic sweetish odor. It can be condensed to a liquid. It burns with a luminous

flame. With oxygen it forms a mixture that explodes when ignited. *Its most characteristic property is its power to unite directly with other substances, particularly with the halogens and with halogen acids.* Thus, it unites with chlorine and bromine, and with hydriodic and hydrobromic acids: —



The products formed with chlorine and bromine are called *ethylene chloride* and *ethylene bromide*. They have been referred to under the head of halogen derivatives of the paraffins. They are isomeric with *ethylidene chloride* and *ethylidene bromide*, which are formed by direct substitution of chlorine or bromine for two hydrogens of ethane or from aldehyde (33).

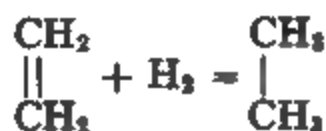
Ethylene combines with hypochlorous acid in aqueous solution to form ethylene chlorhydrin: —



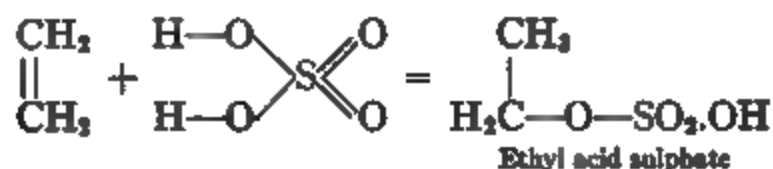
This is frequently used in synthetical work (see glycol and ethylene oxide).

Ethylene combines with sulphur chloride to form mustard gas (79).

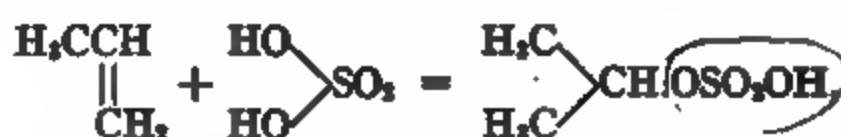
Ethylene combines with hydrogen in the presence of finely divided nickel at  $250^\circ$  to give ethane: —



It combines with sulphuric acid to give ethyl acid sulphate: —



Propylene also combines with sulphuric acid to give isopropyl acid sulphate: —



which decomposes on boiling with water, forming isopropyl alcohol and sulphuric acid (130).

A question that may fairly be asked concerning the structure of ethylene is this: Does it consist of two groups,  $\text{CH}_2$ , or of a methyl group,  $\text{CH}_3$ , and  $\text{CH}$ ? Is it to be represented by the formula  $\text{CH}_2\text{CH}_2$  or  $\text{CH}_3\text{CH}$ ? Perhaps the clearest answer to this question is found in the fact that the chloride formed by addition of chlorine to ethylene, and that formed by replacing the oxygen in aldehyde by chlorine, are not identical. All the evidence is in favor of the view that aldehyde is correctly

represented by the formula  $\text{CH}_3\text{C} \begin{smallmatrix} \text{O} \\ // \\ \text{H} \end{smallmatrix}$ . As has been pointed

out, the chloride obtained from it by the action of phosphorus pentachloride must be represented thus,  $\text{CH}_3\text{CHCl}_2$ . Hence, further, it appears highly probable that the isomeric chloride obtained from ethylene must be represented thus,  $\text{CH}_2\text{Cl.CH}_2\text{Cl}$ . Now, as this substance is formed by direct addition of chlorine to ethylene, ethylene must have the formula  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$ , and not  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH} \end{array}$ .

The fact that it has been impossible to prepare methylene,  $\text{CH}_2$ , the hydrocarbon corresponding to carbon monoxide, may be regarded as a proof that ethylene has the structure represented by the above formula. All attempts to prepare methylene by the abstraction of the halogens from methylene chloride or iodide have given ethylene,  $\text{C}_2\text{H}_4$ , just as attempts to prepare methyl,  $\text{CH}_3$ , have given ethane,  $\text{C}_2\text{H}_6$ . Another proof that ethylene is dimethylene is found in the fact that only one propylene has ever been made, while *three* butylenes are known (see below). It will be recalled that but *two* butanes are possible and known.

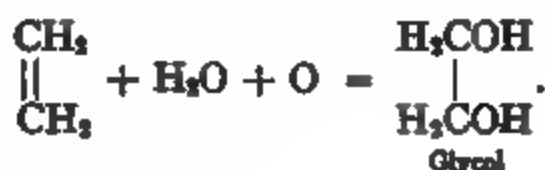
Nothing is known in regard to the relation between the two carbon atoms of ethylene, except that it is probably different from that which exists between the carbon atoms of ethane. It is usually represented by the sign ( $\equiv$ ), or two dots (:);

thus,  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$  or  $\text{CH}_2:\text{CH}_2$ . The question as to the relation between

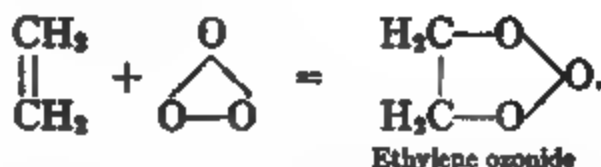
the carbon atoms in ethylene must be left open. If either of the above signs is used, it should serve mainly as an indication of the kind of unsaturation in ethylene, the compound in whose formula it is written having the power to take up two atoms of bromine, a molecule of hydrobromic acid, etc.

All the hydrocarbons of this series with the exception of ethylene polymerize readily. This is also true of some of the halogen derivatives of ethylene. It is a characteristic of unsaturated compounds.

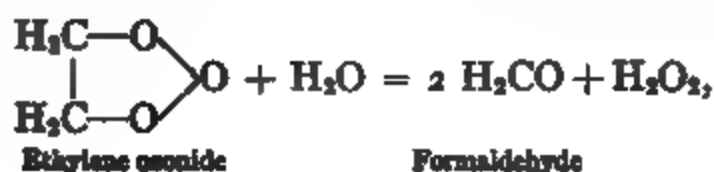
When ethylene is passed into a dilute solution of potassium permanganate it forms glycol:—



With ozone it gives the ozonide:



The formation of ozonides is characteristic of compounds containing the ethylene condition. For each ethylene double bond one molecule of ozone is added. Allyl alcohol and oleic acid both form ozonides. The ozonides are decomposed by water:—



and the products formed show the structure of the unsaturated compound, *e.g.* the formula for oleic acid has been confirmed by the products formed by decomposing oleic acid ozonide with water.

The homologues of ethylene bear the same relation to it that the homologues of ethane bear to this hydrocarbon. Propylene

is methylethylene,  $\begin{array}{c} \text{CH}.\text{CH}_3 \\ || \\ \text{CH}_2 \end{array}$ , just as propane is methylethane,

$\begin{array}{c} \text{CH}_3.\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ . Butylene is dimethylethylene,  $\begin{array}{c} \text{CH}.\text{CH}_3 \\ || \\ \text{CH}.\text{CH}_3 \end{array}$ , or

$\begin{array}{c} \text{C}(\text{CH}_3)_2 \\ || \\ \text{CH}_2 \end{array}$ , or ethylethylene,  $\begin{array}{c} \text{CH}.\text{C}_2\text{H}_5 \\ || \\ \text{CH}_2 \end{array}$ . That is to say, in the

hydrocarbons of the ethylene series the ethylene condition between the carbon atoms occurs only once.

The "official" names of the olefine hydrocarbons end in -ene, *e.g.* ethene, propene, butene, etc. The three butylenes are called 1-butene ( $\text{CH}_3.\text{CH}_2.\text{CH}=\text{CH}_2$ ); 2-butene ( $\text{CH}_3.\text{CH}=\text{CH}.\text{CH}_3$ ); and 2-methylpropene ( $(\text{CH}_3)_2=\text{C}=\text{CH}_2$ ). They are isomeric with tetramethylene (cyclobutane) (304), just as propylene is isomeric with cyclopropane.

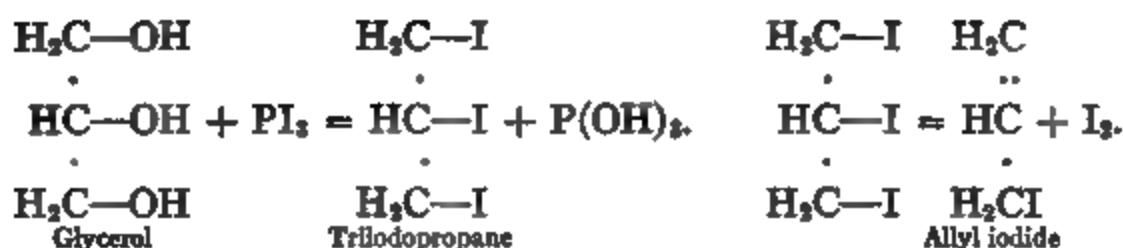
#### ALCOHOLS, $\text{C}_n\text{H}_{2n}\text{O}$

These alcohols bear to the ethylene hydrocarbons the same relation that the alcohols of the methyl alcohol series bear to the paraffins. Only one is well known. This is the second member, corresponding to propylene.

Vinyl alcohol, ethenol,  $\text{H}_2\text{C}=\text{CHOH}$ , is present in crude ether. It goes over into acetic aldehyde,  $\text{CH}_3\text{CHO}$ , very readily.

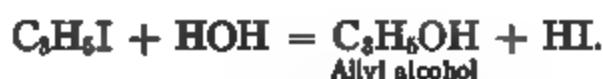
Allyl alcohol, propene-1-ol-3, ( $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$ ), occurs in crude wood spirits. It is formed in several ways from glycerol.

1. By treating glycerol with phosphorus and iodine, allyl iodide is formed. It is probable that the first product of this reaction is triiodopropane:—

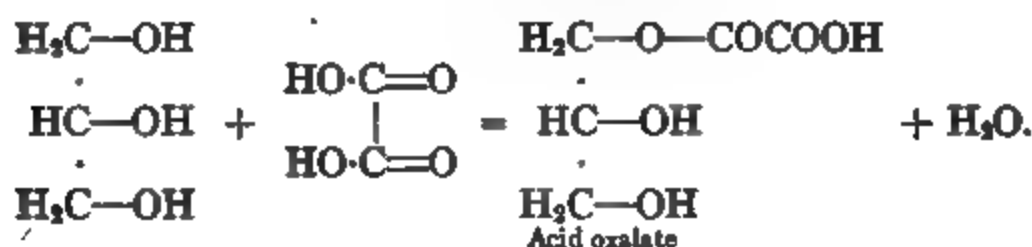


If formed, it at once loses iodine to form allyl iodide as shown above.

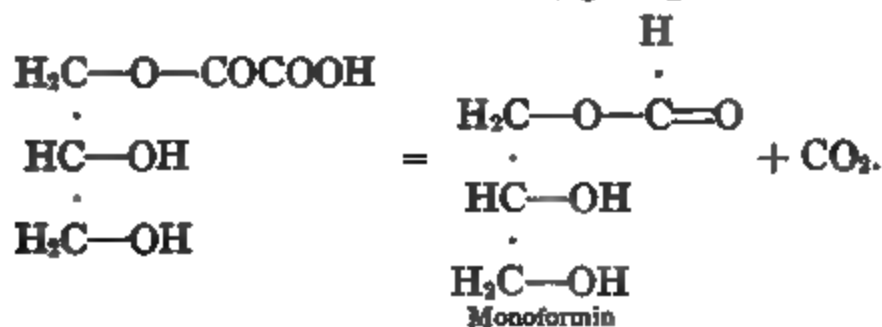
Allyl iodide is converted into the alcohol when boiled with water:—



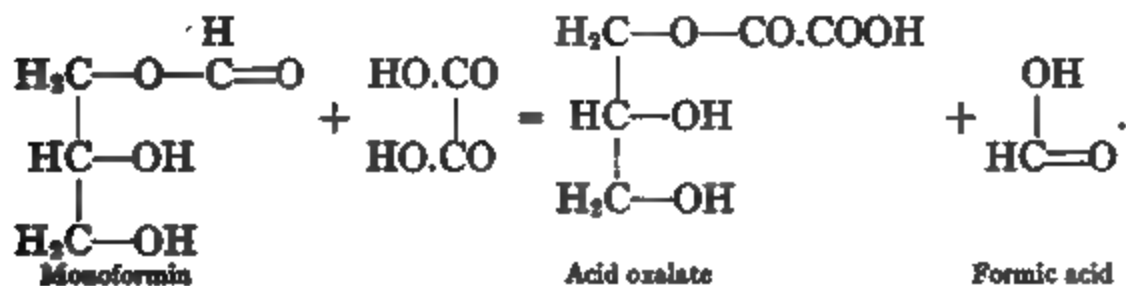
2. Allyl alcohol is also formed by heating glycerol with oxalic acid as in the preparation of formic acid. The first product of this reaction is the acid oxalate:—



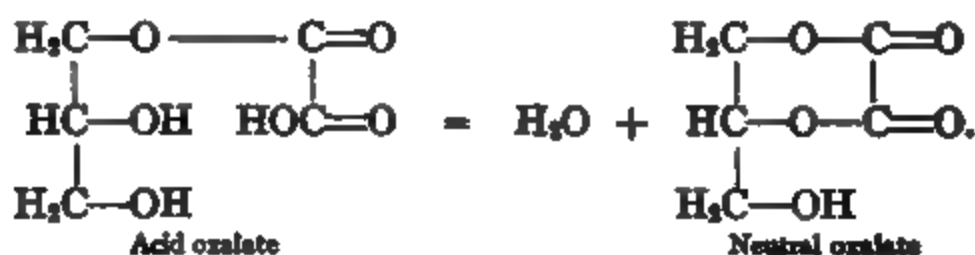
Some of this then loses carbon dioxide, giving monoformin:—



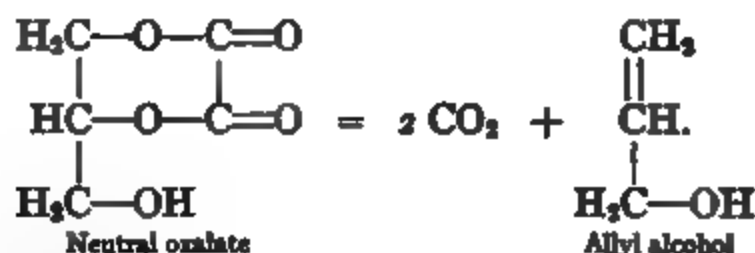
When more oxalic acid is added, as in the preparation of formic acid, formic acid is set free from the monoformin by the stronger oxalic acid, and distills over into the receiver, the acid oxalate being regenerated:—



If no more oxalic acid is added, but the glycerol and oxalic acid are heated to  $220^{\circ}$ – $230^{\circ}$ , the acid oxalate forms the neutral oxalate:—

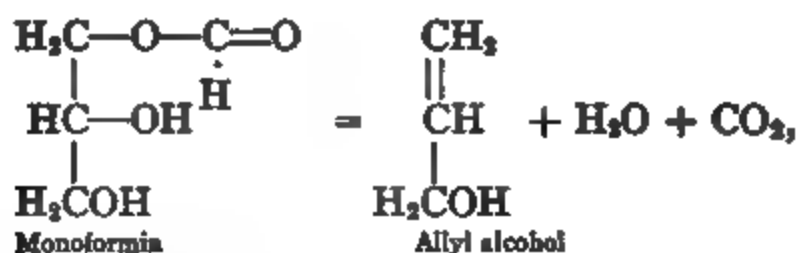


This then loses carbon dioxide and allyl alcohol distils over:—



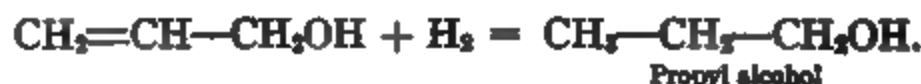
In making allyl alcohol, therefore, it is advisable to use *anhydrous* oxalic acid.

It is probable that some of the allyl alcohol is formed by the decomposition of the monoformin by heat:—



as allyl alcohol is also made by distilling a mixture of glycerol and formic acid.

Allyl alcohol is a colorless liquid boiling at  $96.6^{\circ}$ . It has a disagreeable penetrating odor and is miscible with water in all proportions. Nascent hydrogen converts allyl alcohol into propyl alcohol:—



Allyl alcohol forms esters with acids and gives the other reactions for alcohols. It is, further, a primary alcohol, as it

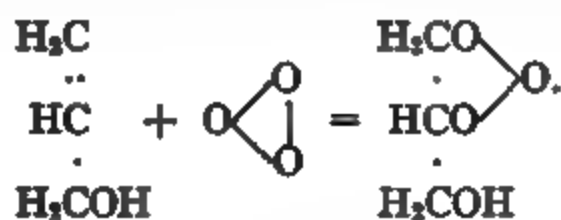
is converted into the corresponding aldehyde (acrolein) and acid (acrylic acid) by oxidation:—



When treated with a 1 per cent solution of potassium permanganate, allyl alcohol is converted into glycerol.

Potassium permanganate is frequently used to determine whether a substance is unsaturated and to determine also the position of the double bond. Unsaturated compounds instantly decolorize a dilute solution of potassium permanganate and two hydroxyl groups are added. The places taken by the two hydroxyl groups indicate the position of the double bond.

Allyl alcohol combines with ozone to give the ozonide:—



**Allyl compounds.**—Among the derivatives of allyl alcohol which are of interest is *allyl sulphide*  $(\text{C}_3\text{H}_5)_2\text{S}$ . It is made artificially by treating allyl iodide with potassium sulphide:—



It is a colorless, oily liquid of a disagreeable odor only slightly soluble in water.

The chief constituent of oil of garlic is *diallyl disulphide*,  $(\text{C}_3\text{H}_5)_2\text{S}_2$ . When this is treated with zinc dust, sulphur is removed, and diallyl sulphide,  $(\text{C}_3\text{H}_5)_2\text{S}$ , results.

**Allyl mustard oil**,  $\text{SCN.C}_3\text{H}_5$ .—Under thiocyanates mention was made of the *isothiocyanates* or *mustard oils*. The thiocyanates of the alcohol radicals are made from potassium thiocyanate. Thus, methyl thiocyanate is made by distilling potassium methyl sulphate and potassium thiocyanate, under reduced pressure:—





The mustard oils (96), on the other hand, are made from carbon bisulphide and substituted ammonias. The chemical reactions of the thiocyanates led to the conclusion that they must be represented by the formula  $\text{NC-SR}$ , while that of the isothiocyanates or mustard oils led to the formula  $\text{SC-NR}$ , as representing their structure. Allyl mustard oil is the chief representative of the class of compounds known as mustard oils. It occurs as a glucoside, sinigrin (530), in black mustard seed. From the glucoside it is set free by the action of an enzyme (myrosin). It also occurs in horse-radish. It is formed by distilling allyl iodide with potassium thiocyanate. If this reaction consisted simply in the substitution of the allyl group  $\text{C}_3\text{H}_5$ , for potassium, the product should be allyl thiocyanate,  $\text{C}_3\text{H}_5\text{S-CN}$ . As a matter of fact it is the isothiocyanate  $\text{C}_3\text{H}_5\text{N-CS}$ . It has been shown, however, that the thiocyanates are converted into the isothiocyanates by heat, so that the formation of the isothiocyanate in this case is not surprising. It is made commercially by this method.

Allyl mustard oil is a liquid, boiling at  $150^\circ$ , and having a very penetrating pungent odor. It blisters the skin. With concentrated sulphuric acid it takes up water, forming allylamine and carbon oxysulphide:—



Zinc and hydrochloric acid convert it into allylamine, and thioformic aldehyde, which at once polymerizes  $(\text{H}_2\text{CS})_2$ :—



These reactions show that in allyl mustard oil the radical allyl is in combination with the nitrogen and not with the sulphur.

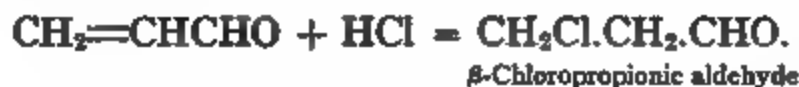
NOTE FOR STUDENT. — What change do the mustard oils in general undergo when treated with nascent hydrogen? What change do the thiocyanates undergo when oxidized and when reduced?

**Acrolein, acrylic aldehyde, propenal,  $\text{CH}_2\text{:CH}\cdot\text{CHO}$ .** — Acrolein can be made by careful oxidation of allyl alcohol. It is

formed by the distillation of impure glycerol and of fats. The glycerol breaks down into water and acrolein:—



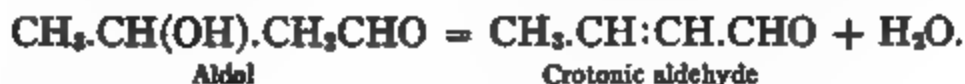
It is best prepared by heating glycerol with concentrated phosphoric acid (sp. gr. 1.17). Acrolein is a volatile liquid which boils at  $52.4^\circ$ . It has an extremely penetrating odor, and its vapor acts violently upon the mucous membrane of the eyes and nose, causing the secretion of tears. Acrolein takes up oxygen from the air, and is converted into the corresponding acid, *acrylic acid*,  $\text{C}_3\text{H}_4\text{O}_2$  (286). It takes up hydrogen, and is thus converted into allyl alcohol and *n*-propyl alcohol. It takes up hydrochloric acid, and is converted into  $\beta$ -chloropropionic aldehyde:—



The first two reactions are characteristic of aldehydes in general; the last one is characteristic of unsaturated compounds of the ethylene series. Acrolein, like ordinary aldehyde, forms polymeric modifications which can easily be reconverted into acrolein by heat. Alkalies resinify it.

It unites with ammonia, forming acrolein ammonia, and with other substances in much the same way as ordinary aldehyde does. With bromine it forms acrolein dibromide, which when treated with barium hydroxide gives *dl*-fructose (232).

Crotonic aldehyde, methyl acrolein,  $\text{CH}_3\text{.CH:CH.CHO}$ . — This aldehyde is most readily made by distilling *aldol* (231):—



When oxidized it gives solid crotonic acid (287), which shows its structure. It is a liquid boiling at  $104^\circ$ – $105^\circ$ .

Crotonic aldehyde is found in crude wood spirits. It reacts in the same way as acrolein does with hydrogen, with oxygen and with hydrochloric acid. Like acrolein it acts violently on the mucous membrane of the eyes and nose, causing the

secretion of tears. It was one of the "tear gases" used during the World War.

ACIDS,  $C_nH_{2n-2}O_2$

Running parallel to the ethylene hydrocarbons, and bearing the same relation to them that the fatty acids bear to the paraffins, is a series of acids of which the first member is acrylic acid,  $C_3H_4O_2$ . The presence of the double bond in these acids makes them stronger acids than the corresponding acids of the fatty acid series containing the same number of carbon atoms. The principal members are named in the subjoined table:—

ACRYLIC ACID SERIES OR OLEIC ACID SERIES

ACIDS,  $C_nH_{2n-2}O_2$

			MELTING POINT	BOILING POINT
Acrylic	acid	$C_3H_4O_2$ . . . .	$13^\circ$	$140^\circ$
Crotonic	"	$C_4H_6O_2$ . . . .	72	182
Angelica	"	$C_5H_8O_2$ . . . .	45	185
Hydrosorbic	"	$C_6H_{10}O_2$ . . . .	Fluid	208
Teracrylic	"	$C_7H_{12}O_2$ . . . .	"	213
Cimic	"	$C_{15}H_{28}O_2$ . . . .	44	
Hypogæic	"	$C_{16}H_{30}O_2$ . . . .	33	
Oleic	"	$C_{18}H_{34}O_2$ . . . .	14	
Erucic	"	$C_{22}H_{42}O_2$ . . . .	33	

Of most of the higher members of the series several isomeric modifications are known. Only a few of these acids will be treated of here.

Acrylic acid, propene acid,  $CH_2:CH.CO_2H$ . — This acid has already been mentioned in connection with hydracrylic acid, which, when heated, breaks down into acrylic acid and water:—



Hydracrylic acid

Acrylic acid

NOTE FOR STUDENT. — This reaction is analogous to that which takes place when ordinary alcohol is converted into ethylene. In what does the analogy consist? What acid is isomeric with hydracrylic acid? How does it conduct itself when heated? Compare the transformation of hydracrylic acid into acrylic acid with that of malic into maleic and fumaric acids, and with that of citric into aconitic acid.

Acrylic acid can be made by careful oxidation of acrolein with silver oxide. The relations between propylene,  $C_3H_6$ , allyl alcohol,  $C_3H_5CH_2OH$ , acrolein,  $C_3H_5CHO$ , and acrylic acid,  $C_3H_5CO_2H$ , are the same as those between any hydrocarbon of the paraffin series, and the corresponding *primary* alcohol, aldehyde, and acid. Acrylic acid can be made also by treating  $\beta$ -iodopropionic acid with alcoholic caustic potash:—



NOTE FOR STUDENT. — Compare this reaction with that by which ethylene is made from ethyl bromide.

Acrylic acid is a liquid having a penetrating odor like that of acetic acid. It boils at  $140^\circ$ , and melts at  $13^\circ$ .

Nascent hydrogen converts it into propionic acid. Hydriodic acid unites directly with it, forming  $\beta$ -iodopropionic acid.

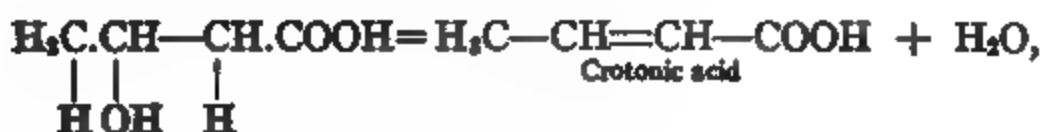
NOTE FOR STUDENT. — What are the analogous reactions with allyl alcohol and acrolein?

**Crotonic acids, butene-2-acids,  $C_4H_6O_2$ .** — Two crotonic acids, the ordinary solid form and liquid isocrotonic acid, occur in croton oil and in crude pyroligneous acid. Ordinary or solid crotonic acid is formed, (1) by hydrolyzing allyl cyanide; (2) by distilling  $\beta$ -hydroxybutyric acid; (3) by treating  $\alpha$ -bromobutyric acid with alcoholic caustic potash; and (4) by heating malonic acid with paraldehyde and acetic anhydride.

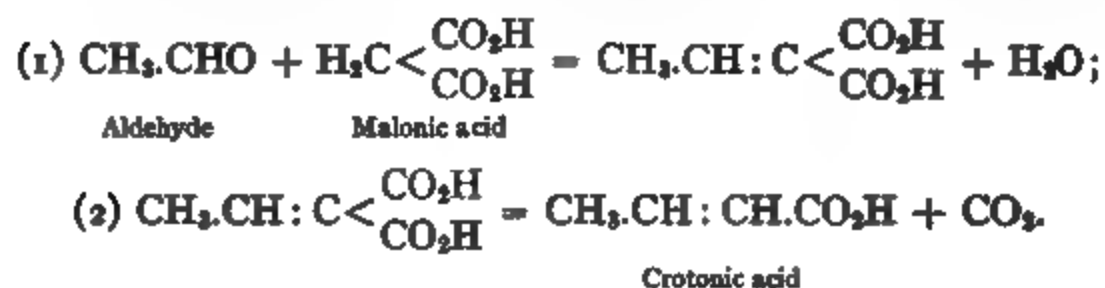
Allyl cyanide has been shown to have the structure,  $CH_2=CHCH_2CN$ , as it is made from allyl bromide,  $CH_2=CHCH_2Br$ , by replacing the bromine by the CN group. When this is hydrolyzed with alkali it gives solid crotonic acid:—



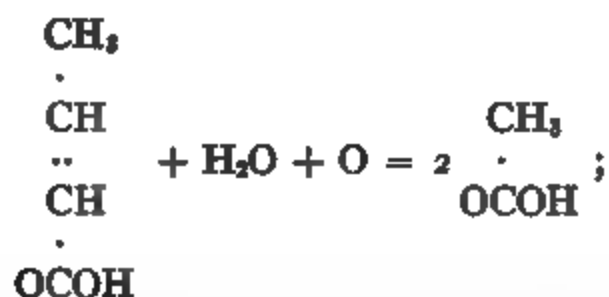
This shifting of the double bond towards the carboxyl group, due to the alkali, is explained by assuming the taking up of water to form  $\beta$ -hydroxybutyric acid:—



and the splitting off of water from the two middle carbon atoms to form crotonic acid as shown above. As crotonic acid can be made also from  $\alpha$ -bromobutyric acid by splitting off hydrobromic acid by means of alkali, this leads to the conclusion that the formula is  $\text{CH}_3.\text{CH}=\text{CH}.\text{COOH}$ . So also the formation of crotonic acid from paraldehyde and malonic acid points to the same formula:—

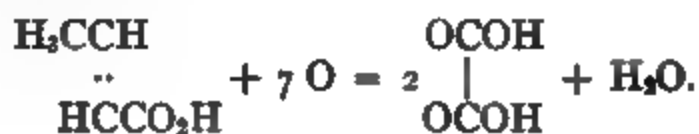


Again, when crotonic acid is fused with caustic potash with access of air, it gives acetic acid as the only product of the oxidation:—



and, as it has been shown that under these circumstances the breaking down occurs at the double bond, this reaction furnishes additional evidence in favor of the view that ordinary crotonic acid has the constitution represented above.

As it has been shown (see above) that the double bond shifts its position towards the carboxyl group in the presence of alkalies this reaction cannot be used to determine the position of the double bond in all cases. Careful oxidation of crotonic acid with potassium permanganate gives oxalic acid, and this is a proof of the position of the double bond:—



Solid crotonic acid melts at  $71^\circ$  and boils at  $189^\circ$ .

**Isocrotonic acid** contains the same groups as crotonic acid, and must be represented by the same structural formula,  $\text{CH}_3\text{CH:CH.CO}_2\text{H}$ , since, like crotonic acid, it gives *n*-butyric acid by reduction and oxalic acid by oxidation with potassium permanganate. It melts at  $15.5^\circ$  and boils at  $169^\circ$ .

As will be shown under maleic and fumaric acids (290), the isomerism of the two forms of crotonic acid is due to the difference in the arrangement of the groups in space. They are stereoisomeric (140).

**Oleic acid,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ .** — This acid was referred to in connection with the fats, being one of the three acids found most frequently in combination with glycerol. Olein, or glyceryl trioleate, is the liquid fat, and is the chief constituent of the fatty oils, such as olive oil, whale oil, etc., and of the fats of cold-blooded animals. It is contained also in almost all ordinary fats. In the preparation of crude stearic acid for the manufacture of candles, the liquid oleic acid is pressed out of the mixture of fatty acids. It is separated from the other fatty acids contained in the liquid by converting the acids into the lead salts and extracting these with ether. Lead oleate is soluble in ether, the other lead salts are not. The oleic acid is obtained from lead oleate by the action of acids.

It is very readily oxidized even by the air and soon turns yellow and acquires a rancid odor. It cannot be distilled without undergoing decomposition except in a vacuum.

When oxidized carefully it gives pelargonic acid,  $\text{CH}_3(\text{CH}_2)_7\text{COOH}$ , and azelaic acid,  $\text{HOOC}(\text{CH}_2)_7\text{COOH}$ , hence the formula must be  $\text{CH}_3(\text{CH}_2)_7\text{CH:CH}(\text{CH}_2)_7\text{COOH}$ .

Sodium oleate forms a *colloidal* solution in water, but in alcohol it forms a *true* solution.

Oleic acid is a colorless oil, insoluble in water, that solidifies when cooled, forming crystals that melt at  $14^\circ$ . It unites with bromine, forming dibromostearic acid. Hydriodic acid converts it into stearic acid: —



Hence it contains a normal chain (see formula above).

Oleic acid combines in the cold with concentrated sulphuric acid to give the sulphuric acid ester of hydroxystearic acid,  $\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{O}.\text{SO}_3\text{H})(\text{CH}_2)_8\text{COOH}$ . When this is boiled with water it gives hydroxystearic acid and sulphuric acid. These reactions take place in the hydrolysis of fats with concentrated sulphuric acid (165).

Oleic acid undergoes a remarkable change when treated with a small quantity of nitrous acid. It is converted into its stereoisomer, elaidic acid, melting at  $44^\circ$ – $45^\circ$ . Triolein undergoes a similar change with nitrous acid and gives the stereoisomer, trielaidin. Trielaidin gives elaidic acid when saponified.

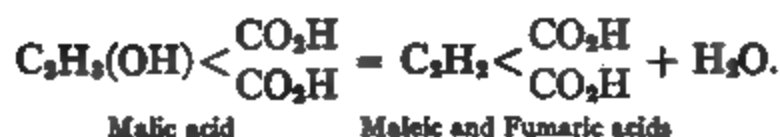
Oleic acid combines very readily with ozone to form an ozonide.

**Hardening of Liquid Fats.**—Liquid fats which consist largely of the glycerol esters of oleic acid and other unsaturated acids can be converted into solid fats (such as stearin) by the addition of hydrogen in the presence of a catalyst (nickel). As the solid fats are much more valuable than the liquid fats this process is carried out on the large scale and is known as the "hardening of oils." These hardened oils are semi-solid, like lard, or solid, like tallow, according as the conversion of the liquid esters (olein, etc.) into stearin is partial or complete. The lard-like compounds (*Crisco*, *Vegetol*, etc.) are used as substitutes for lard in cooking and baking, and large quantities of oleomargarine are thus made from the cheap vegetable oils (cotton-seed oil, cocoanut oil, etc.). Hardened oils are also used in soap and candle making.

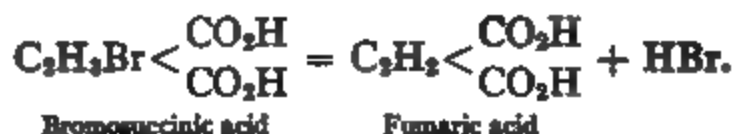
#### POLYBASIC ACIDS OF THE ETHYLENE GROUP

There are a few dibasic acids that bear to the ethylene hydrocarbons the same relations that the members of the oxalic acid series bear to the paraffins. They are to be regarded as derived from the hydrocarbons by the introduction of two carboxyl groups in place of two hydrogen atoms.

**Fumaric and Maleic acids,  $\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$ .**—These acids are formed by distilling malic acid. Fumaric acid remains in the retort; maleic anhydride distils over:—

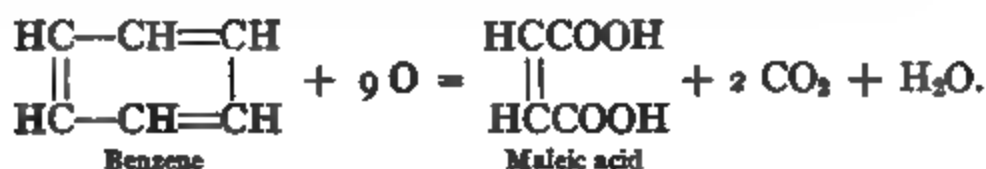


Fumaric acid can also be made by treating bromosuccinic acid with alcoholic potash : —

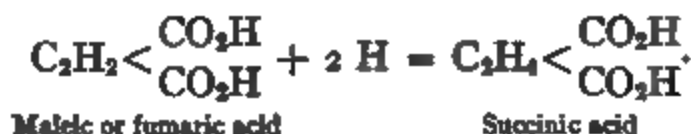


Fumaric acid is frequently found in the plant world. Maleic acid does not occur in nature. Fumaric acid derives its name from its occurrence in the sap of *Fumaria officinalis*.

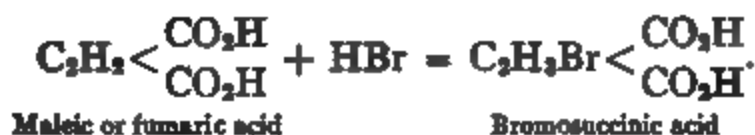
Maleic acid can be obtained in good yield by passing air and the vapor of benzene over vanadium oxide heated to the proper temperature : —



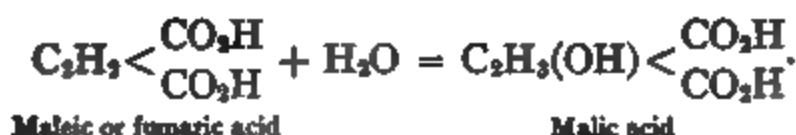
Fumaric acid is only slightly soluble in water; maleic acid is easily soluble. Both fumaric and maleic acids are converted into succinic acid by nascent hydrogen : —



Both are converted into bromosuccinic acid by hydrobromic acid : —



When heated with water in a sealed tube both combine with water to form *dl*-malic acid.





The isomerism disappears when the double bond does. Hence it is due to the presence of the double bond.

They are, therefore, structurally the same, and both must be represented as ethylenedicarboxylic acids  $\begin{array}{c} \text{CHCO}_2\text{H} \\ || \\ \text{CHCO}_2\text{H} \end{array}$ . They are stereoisomeric.

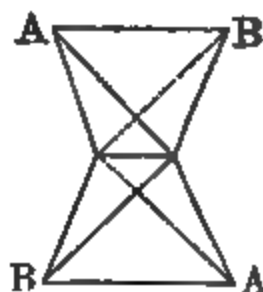
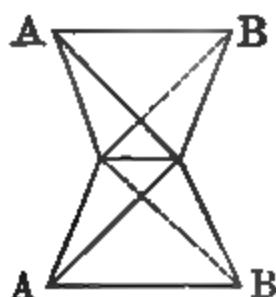
An extension of the fundamental ideas of stereochemistry<sup>1</sup> furnishes an explanation of the isomerism between maleic and fumaric acids. According to these ideas, a carbon atom in combination with four atoms or groups of atoms holds these atoms or groups by bonds directed toward the solid angles of a tetrahedron, the carbon atom itself being at the center of the tetrahedron. When two carbon atoms unite in the simplest way, the stereochemical model representing the compound consists of two tetrahedra united at one of the solid angles of each, thus:—



When two carbon atoms unite by a double bond, as in the ethylene compounds, the model consists of two tetrahedra united by one of the edges of each, thus:—



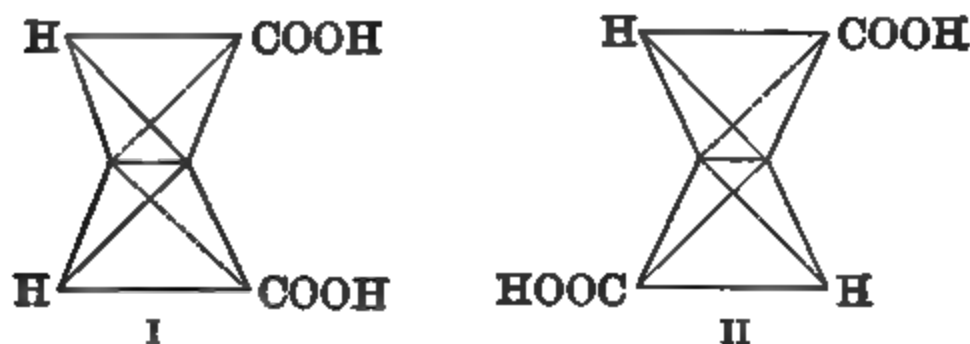
In case each carbon is in combination with two unlike atoms or groups, there are two ways in which these can be arranged in space, as shown by the figures:—



It will be seen that, in the first of these figures, the *A*'s are on one side, and the *B*'s on the other side; while in the second figure *A* and *B* are on one side and *B* and *A* on the other.

<sup>1</sup> See *Stereochemistry*, by A. W. Stewart, p. 109.

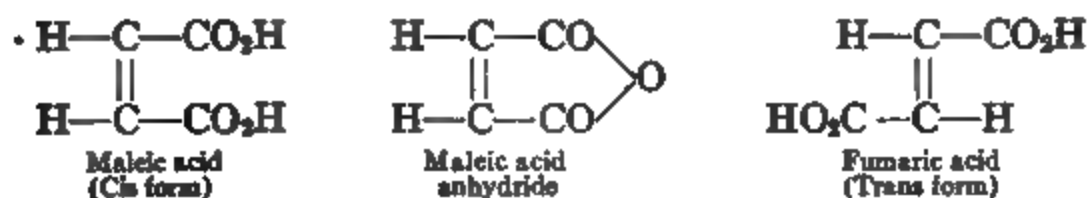
The two arrangements are different. In maleic and fumaric acids each carbon atom is in combination with one hydrogen atom and one carboxyl group, as shown in the above formula. These can be arranged in two ways in space corresponding to the above figures, thus: —



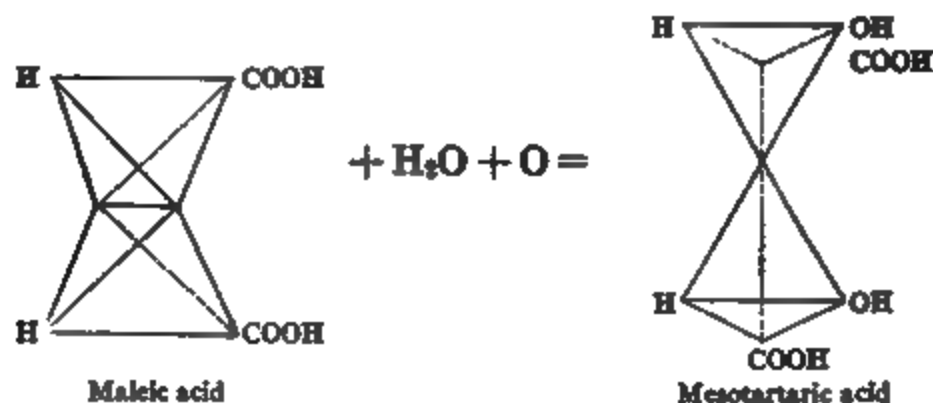
The one having the carboxyl groups on the same side is called the *cis* form, the other with the carboxyl groups on opposite sides is known as the *trans* form (Lat. *cis*, on this side, and *trans*, across).

It is believed that Figure I represents the configuration of maleic acid, and Figure II that of fumaric acid. The main reason for this is the fact that when maleic acid is heated it loses water and forms an anhydride, while fumaric acid does not form an anhydride. As the anhydride is formed by the interaction of the two carboxyl groups, a substance of configuration I could form an anhydride easily because the two carboxyls are near enough to each other to interact and give off water, while in the case of the substance having the configuration represented in Figure II the carboxyls are relatively much farther apart and, for this reason, can not interact in the same way.

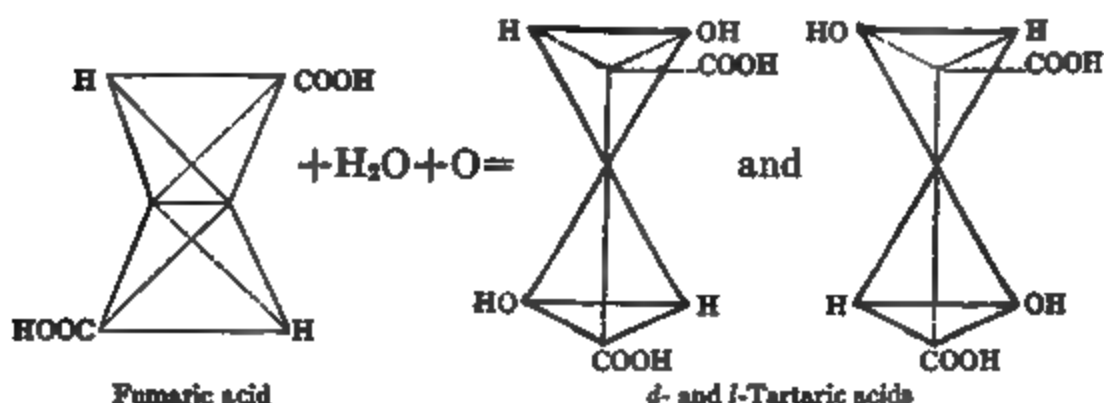
The configurations of maleic acid, its anhydride, and of fumaric acid may be represented by projection formulas, thus: —



Maleic acid gives mesotartaric acid on oxidation with a 1 per cent solution of potassium permanganate : —



while fumaric acid gives racemic acid : —



The presence of the double bond increases the strength of the acids. Thus fumaric acid is about 14 times as strong as succinic acid, while maleic acid is about 12 times as strong as fumaric acid, probably because of the proximity of the carboxyl groups. (Compare the strength of oxalic acid with that of malonic and succinic acids.)

The two crotonic acids already referred to are believed to be related to each other in the same way as maleic and fumaric acids, as shown by the projection formulas : —



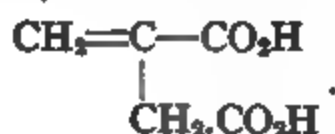
**Acids, C<sub>5</sub>H<sub>6</sub>O<sub>4</sub>.** — When citric acid is rapidly heated, a distillate consisting of the anhydrides of two acids of the formula C<sub>5</sub>H<sub>6</sub>O<sub>4</sub> is obtained. These acids are *itaconic* and *citraconic*

*acids.* When itaconic anhydride is distilled under ordinary pressure, it is converted into citraconic anhydride. When citraconic anhydride is heated for some time with water at  $150^{\circ}$ , itaconic acid is formed. When a water solution of citraconic acid is treated with hydrochloric or nitric acid and then evaporated, a third acid, *mesaconic acid*, isomeric with citraconic and itaconic acid, is obtained.

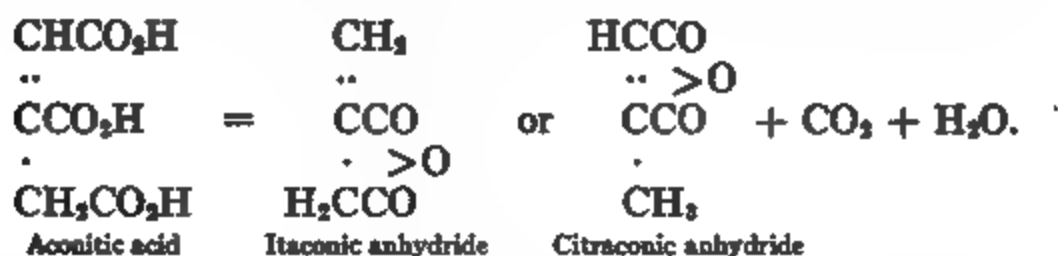
It has been shown that citraconic and mesaconic acids are respectively homologues of maleic and fumaric acids, as represented by the projection formulas:—



Like fumaric acid, mesaconic acid does not form an anhydride. Itaconic acid is methylenesuccinic acid:—



The formation of itaconic and citraconic anhydrides from aconitic acid, the first product formed when citric acid is heated, is shown thus:—



**Aconitic acid,  $\text{C}_6\text{H}_5\text{O}_6$ ,  $\text{C}_2\text{H}_3(\text{CO}_2\text{H})_3$ .**—Aconitic acid is the only tribasic acid of this group that need be mentioned. It is formed when citric acid is heated to  $175^{\circ}$ . It is found in nature in aconite root, and in the sap of sugar cane and of the beet.

Nascent hydrogen converts it into tricarballic acid,  $\text{C}_2\text{H}_3(\text{CO}_2\text{H})_3$  (173). Its structural formula is given above.

### ACETYLENE AND ITS DERIVATIVES

The principal reactions by means of which it is possible to pass from a hydrocarbon of the paraffin series to the corresponding hydrocarbon of the ethylene series consist in introducing a halogen into the paraffin, and then treating the mono-halogen substitution product with alcoholic caustic potash : —



The effect of these two reactions is the abstraction of two hydrogen atoms from the paraffin. The following questions therefore suggest themselves : —

Suppose a dibromo substitution product of a paraffin should be heated with alcoholic caustic potash ; will the effect be that represented by the equation,



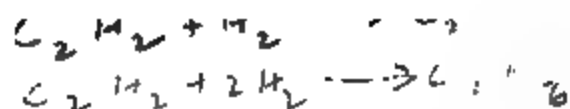
And, further, suppose a monobromo substitution product of an ethylene hydrocarbon is heated with alcoholic potash ; will the effect be that represented by the equation,



If so, it is plain that we have it in our power to make a new series of hydrocarbons, the members of which must bear to the ethylene hydrocarbons the same relation that the latter bear to the paraffins. The general formula of this series would be  $\text{C}_n\text{H}_{2n-2}$ , that of the ethylene series being  $\text{C}_n\text{H}_{2n}$ , and that of the paraffin series,  $\text{C}_n\text{H}_{2n+2}$ .

A few members of the hydrocarbon series,  $\text{C}_n\text{H}_{2n-2}$ , are known, though only one is well known, and this one alone need be taken up here.

**Acetylene, ethine,  $\text{C}_2\text{H}_2$ .** — Acetylene is contained in coal gas in small quantity. It is formed by direct combination of hydrogen and carbon when a current of hydrogen is passed between incandescent carbon poles ; when alcohol, ether, methane, and other organic substances, are passed through a tube heated to redness ; when coal gas and some other sub-



## ACETYLENE, ETHINE

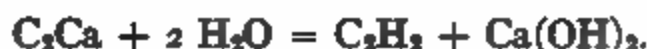
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stances are burned in an insufficient supply of air, as when a bunsen burner "strikes back"; and when ethylene bromide is treated with alcoholic caustic potash:—



It is formed further when bromoform,  $CHBr_3$ , or iodoform,  $CHI_3$ , is treated with silver or zinc dust. (Write the equations.)

It is easily made by the action of water on calcium carbide:—



This process is extensively used on the large scale for the preparation of acetylene for illuminating and other purposes.

Acetylene is a colorless gas of unpleasant odor when impure. When perfectly pure it is said to have a pleasant, ethereal odor. It is poisonous. It burns with a luminous, sooty flame. It is somewhat soluble in water, but more soluble in organic solvents. One volume of acetone dissolves 25 volumes of acetylene at ordinary pressure and 300 volumes at 12 atmospheres. This solution in steel cylinders and under pressure (*Prestolite*) is frequently used instead of acetylene itself for illuminating purposes and in acetylene torches. Acetylene when burned in specially constructed acetylene burners gives a very brilliant light without smoke. When burned with oxygen in a blow-pipe similar to the oxyhydrogen blowpipe, it gives a very hot flame. This is used for autogenous welding of steel and aluminium, for making repairs in iron and steel vessels, for cutting steel and for glass blowing, especially with pyrex glass.

When heated to a sufficiently high temperature, acetylene is converted into its polymers, benzene,  $C_6H_6$ , and styrene,  $C_8H_8$ . It unites with hydrogen to form ethylene and ethane. It unites with nitrogen, under the influence of the sparks from an induction coil, forming hydrocyanic acid:—



Acetylene forms some interesting compounds with metals. Among them may be mentioned the copper compound formed

by the action of acetylene on an ammoniacal solution of cuprous chloride. This is used as a means of detecting acetylene. It has the composition  $C_2Cu_2$ , and is the cuprous salt of acetylene. It is a reddish brown substance, insoluble in water. When dry, it explodes violently at  $120^\circ$ . Hydrochloric acid decomposes it, acetylene being evolved. (Write the equations.)

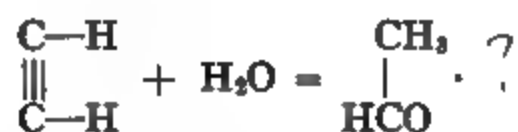
Acetylene acts like a weak dibasic acid. Cuprous carbide,  $C_2Cu_2$ , calcium carbide,  $C_2Ca$ , silver carbide,  $C_2Ag_2$ , etc., are salts of the acid.

*Calcium carbide*,  $CaC_2$ , is formed by heating coal and lime together in the electric furnace.

Acetylene unites with chlorine and with bromine, forming the compounds  $C_2H_2Cl_4$  and  $C_2H_2Br_4$ , tetrachloro- and tetrabromoethane. It unites with hydrobromic and hydriodic acids, forming disubstitution products of ethane:—



In the presence of yellow mercuric oxide and 6 per cent sulphuric acid acetylene combines with water to form acetic aldehyde:—

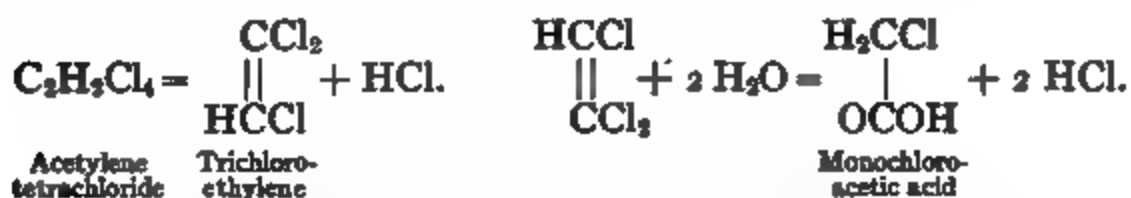


The acetic aldehyde is very pure and can be oxidized by the air in the presence of a suitable catalyst (manganese acetate) to acetic acid. The acetic acid made in this way is free from water and other impurities. Large quantities of acetic acid were made in this way, from acetylene, in Canada during the World War. The capacity of the plant is more than 50 tons of glacial acetic acid per day. The acetic acid was vaporized and passed through a tube heated to  $485^\circ$  containing the catalyst, hydrated lime, and thus converted into acetone:—



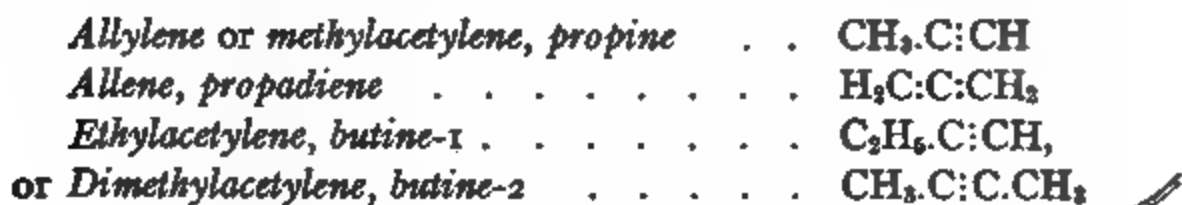
Ten tons a day of acetone of great purity were thus produced. The acetone was used in the manufacture of *cordite*; the

acetic acid to make cellulose acetate used as a varnish for the wings of airplanes. It is said that monochloroacetic acid (63) is made on the large scale in France from acetylene, chlorine, and water. Acetylene tetrachloride is first made (see above). This readily loses hydrochloric acid and gives trichloroethylene. The trichloroethylene when passed into 90 per cent sulphuric acid gives monochloroacetic acid : —



The union between the carbon atoms in acetylene is commonly represented by three lines ( $\equiv$ ), or three dots ( $:$ ). Thus, acetylene is written  $\text{HC}\equiv\text{CH}$  or  $\text{CH}:\text{CH}$ . Like the sign of the ethylene condition, the sign of the acetylene condition should not be interpreted too literally. It is best to regard it as the sign of the condition existing in acetylene. *This condition carries with it the power to take up four atoms of a halogen, or two molecules of hydrobromic acid and similar acids.*

Most of the higher members of the acetylene series of hydrocarbons bear to acetylene the same relation that the higher members of the ethylene series bear to ethylene.



**Allylene** is made from propylene bromide. It resembles acetylene very closely. Sulphuric acid polymerizes it to mesitylene (324).

**Allene**, **propadiene**,  $\text{H}_2\text{C}:\text{C}:\text{CH}_2$ , is made by the electrolysis of itaconic acid. It is a gas. It does not yield copper and silver compounds as allylene does. It is a diethylene compound.

**Dimethylacetylene**,  $\text{H}_3\text{C}.\text{C}\equiv\text{C}.\text{CH}_3$ , does not form copper or silver salts.

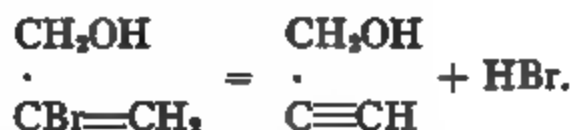


The homologues of acetylene may be divided into two classes:

1. Those which are obtained from acetylene by the replacement of one or both of the hydrogen atoms by saturated radicals, such as methyl, ethyl, etc. These are called the *true homologues*. They all retain the condition peculiar to acetylene.

2. Those in which the ethylene condition occurs twice, as in the hydrocarbons, *allene*,  $\text{H}_2\text{C}:\text{C}:\text{CH}_2$ , and *butadiene-1,3*,  $\text{H}_2\text{C}:\text{CH}:\text{CH}:\text{CH}_2$ . These are called *diethylene derivatives*. Like acetylene and its true homologues, they have the power to take up four atoms of a halogen, or two molecules of hydrobromic acid and similar acids, but they do not form copper and silver salts. In fact, not all true homologues of acetylene have this power, for example, dimethylacetylene,  $\text{H}_3\text{CC}:\text{CCH}_3$ . It is necessary that an acetylene hydrogen atom should be present.

**Propargyl alcohol, propine-1-ol-3**,  $\text{C}_3\text{H}_4\text{O}$ . — This primary alcohol is mentioned merely as an example of alcohols which are derived from the acetylene hydrocarbons. It is the hydroxyl derivative of allylene, or methylacetylene. It is made by treating bromoallyl alcohol,  $\text{C}_3\text{H}_4\text{BrOH}$ , with aqueous caustic potash: —

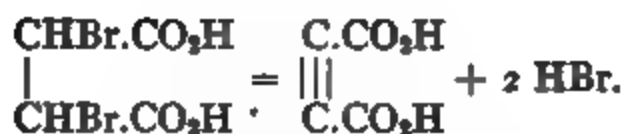


Like acetylene it forms copper and silver salts.

#### ACIDS, $\text{C}_n\text{H}_{2n-4}\text{O}_2$

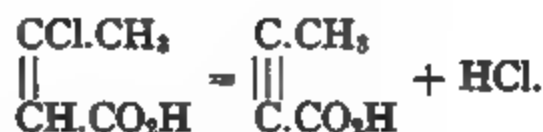
These acids are the carboxyl derivatives of the acetylene hydrocarbons, and hence differ from the members of the acrylic acid series by two atoms of hydrogen each, and from the members of the fatty acid series by four atoms of hydrogen each.

**Propiolic acid, propine acid**,  $\text{C}_3\text{H}_2\text{O}_2$ ,  $\text{HC}\equiv\text{CCO}_2\text{H}$ . — The potassium salt of this acid has been made from the acid potassium salt of acetylenedicarboxylic acid,  $\text{KO}_2\text{CC}\equiv\text{CCO}_2\text{H}$ , by heating its aqueous solution, carbon dioxide being eliminated. *Acetylenedicarboxylic acid* (*butine diacid*) is formed by heating dibromosuccinic acid with a water solution of caustic potash: —



It is a very strong dibasic acid, having about the strength of sulphuric acid, thus showing the remarkable effect of the triple bond.

Tetrolic acid,  $\text{C}_4\text{H}_4\text{O}_2$ ,  $\text{H}_3\text{C.C}\equiv\text{C.CO}_2\text{H}$ , is obtained by treating  $\beta$ -chlorocrotonic acid with caustic potash:—



It can also be made from crotonic acid:—



**Sorbic acid**,  $\text{C}_6\text{H}_8\text{O}_2$ ,  $\text{CH}_2\text{:CH:CH:CH:CH.CO}_2\text{H}$ .—This acid occurs in the juice of the unripe sorb apple. It takes up hydrogen and yields *hydrosorbic acid*, a member of the acrylic acid series (286). It also takes up bromine, the final product of the action being tetrabromocaproic acid,  $\text{C}_6\text{H}_7\text{Br}_4\text{CO}_2\text{H}$ . With hydrobromic acid it forms dibromocaproic acid:—



It will be observed that sorbic acid is a diethylene derivative and that it does not contain the acetylene condition.

**Linolic acid**,  $\text{C}_{17}\text{H}_{31}\text{O}_2$ , and **linolenic acid**,  $\text{C}_{17}\text{H}_{29}\text{O}_2$ , occur in the form of esters of glycerol (linolin and linolenin) in the *drying oils* such as linseed oil and hemp seed oil. They are obtained from these oils by saponification with alkalies, and decomposition with acid of the soaps formed. They are oily liquids, the most marked property of which is their power to take up oxygen from the air and turn into solid substances. Linseed oil itself has this property of taking up oxygen and

hardening or drying in the air, and for this reason it is very extensively used as a constituent of varnishes and of oil paints, and in the manufacture of linoleum. When heated alone in the absence of air, linseed oil undergoes polymerization and becomes thick and viscous. This *litho oil*, as it is called, is used in lithographic printing, and in the manufacture of printers' ink.

Both these acids yield stearic acid on reduction. With bromine linolic acid gives a tetrabromide, linolenic acid a hexabromide. On oxidation linolic acid gives caproic acid,  $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ , oxalic acid and azelaic acid,  $(\text{CH}_2)_7(\text{CO}_2\text{H})_2$ , which leads to the formula:—

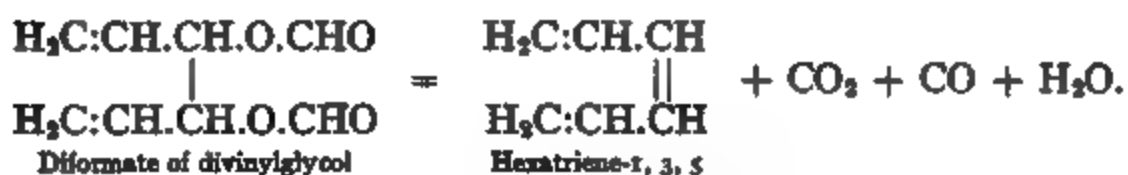


Linolenic acid, which is present in linseed oil in much larger quantity than linolic acid, has been shown in a similar manner to have the structure represented by the formula:—



#### HYDROCARBONS, $\text{C}_n\text{H}_{2n-4}$

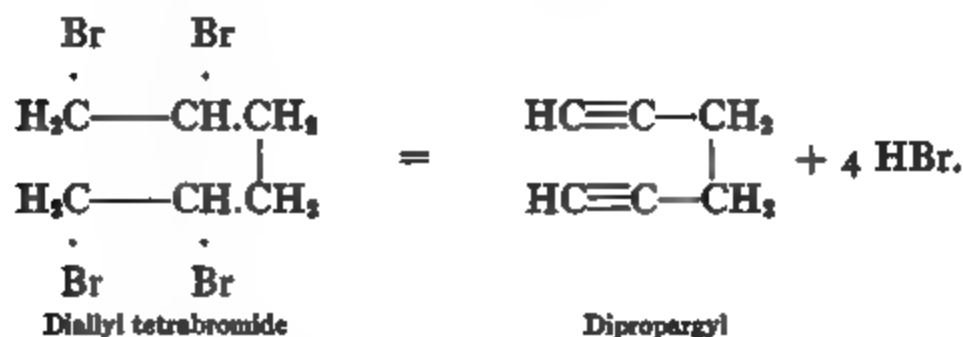
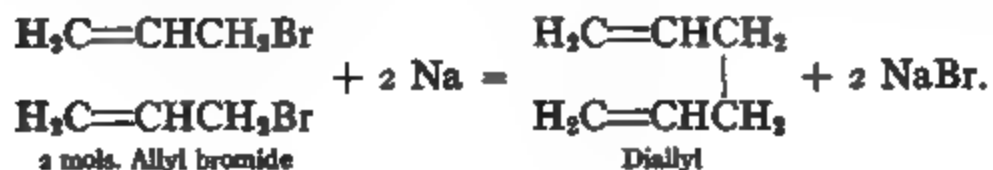
Hexatriene-1, 3, 5,  $\text{C}_6\text{H}_8$ , is formed by heating the diformate of divinylglycol to  $165^\circ\text{--}200^\circ$ :—



It is a fluid boiling at  $77.5^\circ\text{--}79^\circ$ . It takes up six atoms of bromine to form a hexabromide, thus showing the presence of three double bonds. When reduced with hydrogen in the presence of nickel it gives *n*-hexane,  $\text{C}_6\text{H}_{14}$ . Hydrocarbons isomeric with hexatriene as well as homologues of hexatriene are also known.

HYDROCARBONS,  $C_nH_{2n-6}$ 

Dipropargyl, hexadiene-1, 5,  $C_6H_6$ , is made from diallyl tetrabromide by the action of alcoholic potash. The diallyl tetrabromide is made from diallyl, which in turn is made from allyl bromide and sodium:—

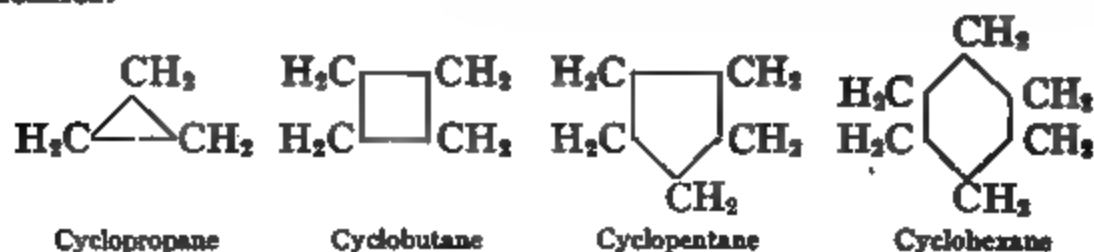


It is a liquid boiling at  $85.4^\circ$ . It combines with bromine with explosive violence. Like acetylene it gives copper and silver compounds, and from its method of formation it must contain the acetylene condition twice. It is isomeric with benzene. Other isomers of dipropargyl are also known.

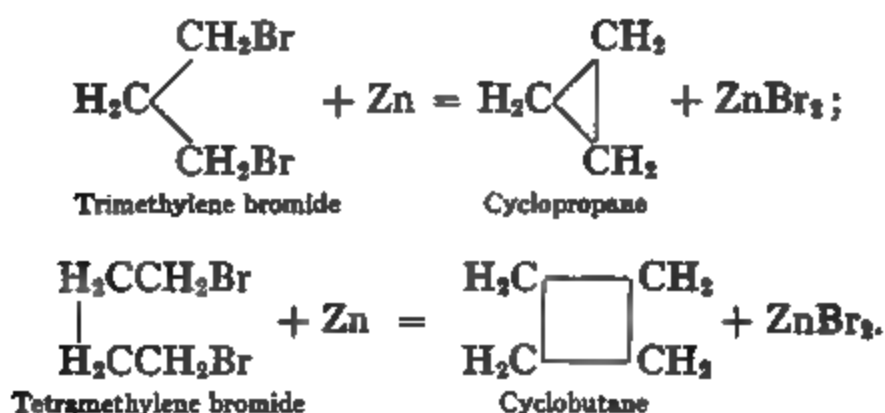
## CHAPTER XIV

### CARBOCYCLIC COMPOUNDS

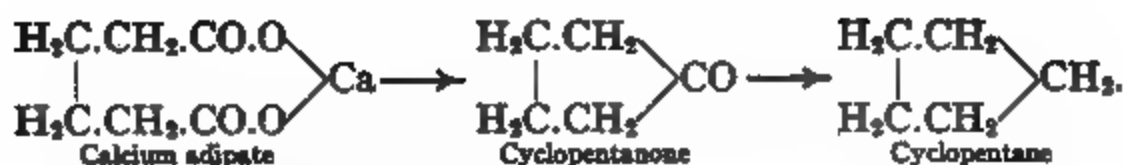
The compounds thus far dealt with may all be derived from marsh gas, or they are *methane derivatives*. Most of them have an *open chain* formula; a few, like succinic acid anhydride, the purine derivatives, etc., have a *closed chain* structure. Besides the methane derivatives there is another great class of organic compounds which have the closed chain structure, or are cyclic compounds. Of these the simplest are cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc., isomeric with the olefines.



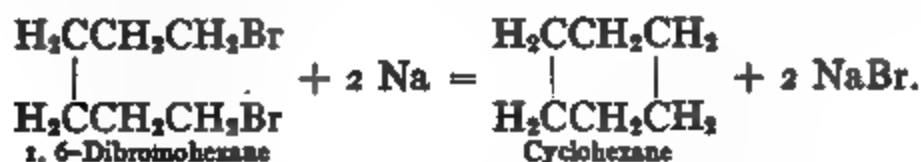
They are made by the abstraction of bromine from compounds like trimethylene bromide and tetramethylene bromide by sodium or zinc:—



Cyclopentane is most readily made by reducing the ketone, cyclopentanone, which results from the dry distillation of calcium adipate:—



Cyclohexane has been made from 1, 6-dibromohexane by abstracting bromine by means of sodium: —



Cyclohexane and its derivatives are most readily formed by reducing benzene and its derivatives (328).

These hydrocarbons resemble the paraffins in their chemical properties and hence their names. The derivatives closely resemble the corresponding derivatives of the paraffins.

The cyclic hydrocarbons up to cyclooctane have been made synthetically. The following table gives the boiling points of these hydrocarbons together with those of the normal hydrocarbons of the paraffin and olefine series having the same number of carbon atoms.

PARAFFINS	BOILING PT.	OLEFINES	BOILING PT.	CARBOCYCLIC	BOILING PT.
$\text{C}_3\text{H}_8$	-44.1°	$\text{C}_3\text{H}_6$	-47°	$\text{C}_3\text{H}_6$	-34°
$\text{C}_4\text{H}_{10}$	-0.3	$\text{C}_4\text{H}_8$	1-1.5	$\text{C}_4\text{H}_8$	11-12
$\text{C}_5\text{H}_{12}$	36.4	$\text{C}_5\text{H}_{10}$	39-40	$\text{C}_5\text{H}_{10}$	50.2-50.8
$\text{C}_6\text{H}_{14}$	69	$\text{C}_6\text{H}_{12}$	67.7	$\text{C}_6\text{H}_{12}$	80.75
$\text{C}_7\text{H}_{16}$	98.4	$\text{C}_7\text{H}_{14}$	98-99	$\text{C}_7\text{H}_{14}$	117
$\text{C}_8\text{H}_{18}$	125.5	$\text{C}_8\text{H}_{16}$	124	$\text{C}_8\text{H}_{16}$	147

It will be noted that, while the paraffins and the olefines containing the same number of carbon atoms have nearly the same boiling points, those of the corresponding cyclic hydrocarbons are higher than either.

The most important of the carbocyclic compounds are the benzene derivatives.

## CHAPTER XV

### THE BENZENE SERIES OF HYDROCARBONS, $C_nH_{n-6}$ , AROMATIC COMPOUNDS

The hydrocarbons of this series (see table below) are all derived from benzene,  $C_6H_6$ , in the same way that the paraffin hydrocarbons are derived from marsh gas, *i.e.*, they are alkyl derivatives of benzene. When bituminous or soft coal is heated to a high temperature for the purpose of manufacturing coal gas (illuminating gas) or in the manufacture of coke, benzene and several of its homologues are formed and are found both in the gases and in the *coal tar* which results. Practically all the benzene hydrocarbons and some of their derivatives are thus obtained from soft coal, either as a by-product of the coking ovens or in the manufacture of coal gas. In making coal gas, the coal is heated in sealed retorts and all the products pass through condensers in which a thick, black, tarry liquid, *coal tar*, collects. This coal tar was originally thrown away or burned as fuel, until it was found to contain valuable benzene compounds, which could be obtained from it by distillation. It is an extremely complex mixture of aromatic compounds from which a great many substances (mainly hydrocarbons) have been isolated. The most important substances obtained from coal tar are naphthalene and anthracene, in addition to smaller quantities of the hydrocarbons of the benzene series, and also phenol, cresols, pyridine, quinoline and carbazole. The tar is distilled from large fire-heated stills.

When the tar is distilled completely to a hard pitch the distillate is usually collected in several fractions as follows:—

1. Light oil or crude naphtha fraction up to about  $110^\circ$ .
2. Acid oil and naphthalene fraction from  $110^\circ$  to  $205^\circ$ .
3. Creosote oil fraction from  $205^\circ$  to  $270^\circ$ .
4. Anthracene oil fraction from  $270^\circ$  to  $355^\circ$ .
5. Heavy oil fraction from  $355^\circ$  to  $450^\circ$ .

The light oil is distilled for the purpose of obtaining benzene, toluene, and the xylenes, while the acid oil fraction is allowed to cool and the crude naphthalene that crystallizes out is removed by means of centrifugals. The clear oil is then treated with a solution of sodium hydroxide to remove acids (phenol or carbolic acid, the cresols, etc.). The creosote oil fraction is used for the preservation of wood. The anthracene oil fraction is cooled to separate anthracene and carbazole, which are filtered off, and the oil left is used for the same purpose as the creosote oil.

Most of the benzene hydrocarbons are now obtained from the gases of the coking ovens. These gases, after being separated from the tar, are passed through a weak solution of sulphuric acid to remove ammonia (and pyridine) and then through large scrubbing towers, in which they are brought into intimate contact with a stream of scrubbing oil, flowing counter-current to the gas. The scrubbing oil used in this country is a high boiling petroleum fraction known as "straw oil." It abstracts the aromatic hydrocarbons from the gases. When saturated, the straw oil from the scrubbing towers passes into a still in which steam is blown through the oil in order to distil the aromatic hydrocarbons. This distillate forms the crude "gas benzol" or "coke-oven light oil" of commerce. It is the principal source of benzene, toluene, the xylenes, and other more volatile aromatic hydrocarbons. This coke-oven light oil is distilled through fractionating columns and "crude benzol," "crude toluol," "crude solvent naphtha" (mostly xylenes) and "crude heavy solvent naphtha" (mostly trimethylbenzenes and indene) are obtained. The crude benzol, crude toluol, and crude solvent naphtha are purified by agitating them with sulphuric acid, washing with water and then agitating with a solution of caustic soda and again washing with water. They are finally distilled through fractionating columns and separated into the various grades of benzene, toluene, xylenes, and refined solvent naphtha found in commerce.<sup>1</sup>

Some of the principal members of this series of hydrocarbons with their boiling points and melting points are given in the table below: —

#### HYDROCARBONS OF THE BENZENE SERIES, $C_nH_{2n-6}$

NAME	FORMULA	MELTING POINT	BOILING POINT
Benzene	$C_6H_6$	5.48°	80.2°
Toluene	$C_6H_5.CH_3$	-94.5	110.7
<i>o</i> -Xylene	$C_6H_4(CH_3)_2(o)$	-45.00	144.4
<i>m</i> -Xylene	$C_6H_4(CH_3)_2(m)$	-53.60	139.
<i>p</i> -Xylene	$C_6H_4(CH_3)_2(p)$	16.00	138.2

<sup>1</sup> See *Coal Tar and Ammonia*, by George Lunge, Fifth Edition, 1916.





Benzene was obtained in this way by Mitscherlich in 1833 from benzoic acid obtained from gum benzoin, a plant product. Benzene has also been made by the polymerization of acetylene by heat (311):—



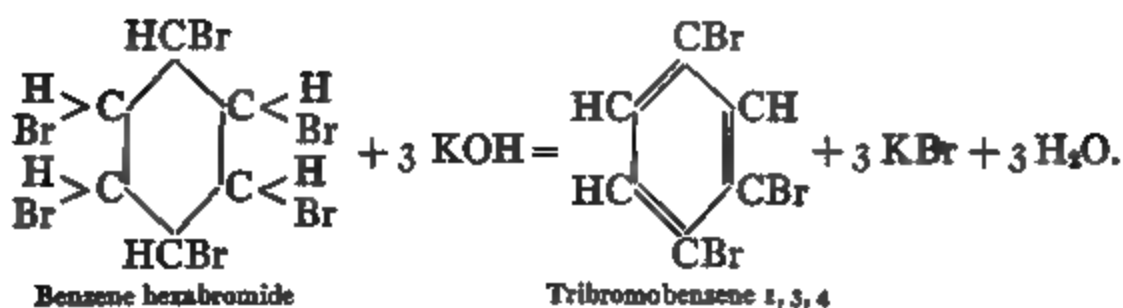
and also from cyclohexane (310).

To purify the hydrocarbon obtained from light oil by fractional distillation, it is crystallized by cooling to  $0^\circ$  and the fluid portion removed by filtration. Only benzene crystallizes at this temperature, toluene and the other homologues remain liquid. When benzene free from *thiophene*,  $\text{C}_4\text{H}_4\text{S}$ , (a substance always present in coal tar benzene) is required, it is boiled with aluminium chloride and then distilled from the chloride, or the thiophene is removed by repeated agitation with concentrated sulphuric acid. The thiophene is more readily sulphonated than benzene, and the thiophenesulphonic acid dissolves in the sulphuric acid. Perfectly pure benzene can also be obtained by the distillation of *pure* benzoic acid with lime.

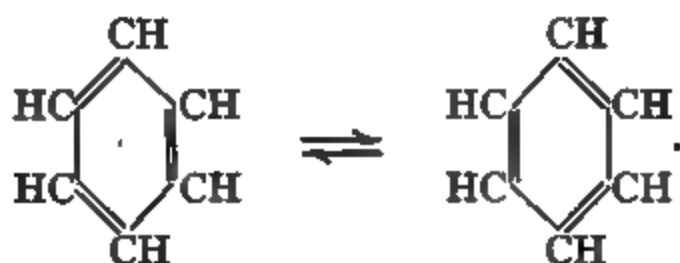
Benzene is a colorless liquid. It boils at  $80.2^\circ$  and has a peculiar, pleasant odor. Several of the derivatives and homologues of benzene have an aromatic odor and hence the name *aromatic* compounds was given to them originally to distinguish them from the fatty compounds, and it is still in general use. Benzene is lighter than water. Its specific gravity at  $20^\circ$  compared with water at  $4^\circ$  is 0.8799. It is slightly soluble in water and it dissolves a small quantity of water. It is soluble in alcohol, in ether, and in chloroform. It burns with a bright, luminous, smoky flame. It crystallizes in orthorhombic prisms which melt at  $5.48^\circ$ . It is an excellent solvent for oily and resinous substances and for many other organic compounds. It is used in making chlorobenzene, nitro and dinitrobenzene, and in making benzene mono and disulphonic acids. Large quantities are used in making synthetic indigo (484). A large part of it is used as a fuel in motors. In this case the crude benzol (50–90 per cent benzene) is used.

Benzene and the other substances obtained from coal tar or light oil by distillation are known as "crudes" or "coal-tar





These facts show that benzene is a closed chain or cyclic compound consisting of six CH groups and make it appear probable that it contains three double bonds as shown in the formula:—

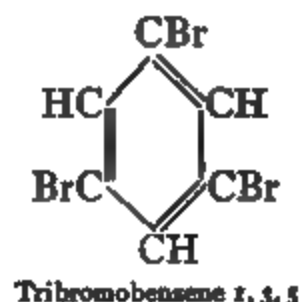
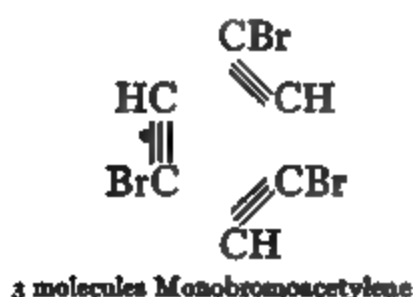


It is, therefore, cyclohexatriene. This formula for benzene was first proposed in 1865 by August Kekulé, and it has played an exceedingly important part in the development of the chemistry of the benzene compounds.

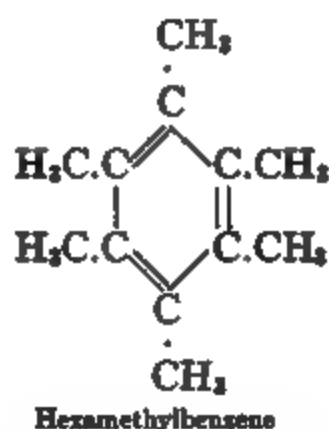
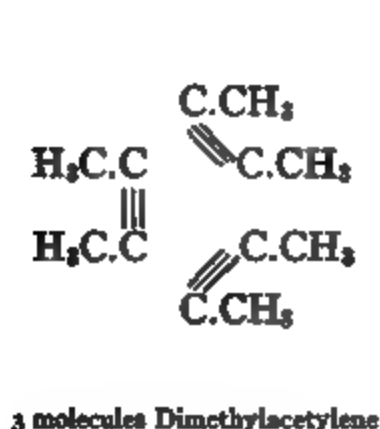
This formula is also in accord with the synthesis of benzene and its derivatives from acetylene and the substituted acetylenes. Thus three molecules of acetylene condense to one of benzene:—



This reaction is a reversible one, and so the conversion of the acetylene into benzene is never complete. When passed through a red hot tube, benzene is partially converted back into acetylene. Monobromoacetylene polymerizes in the light to tribromobenzene:—



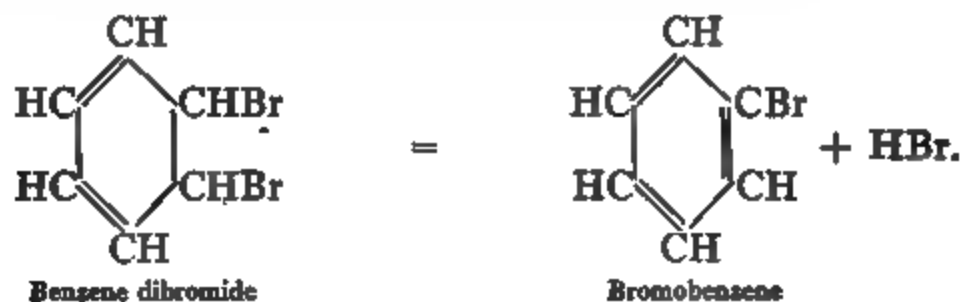
Methylacetylene and dimethylacetylene give trimethylbenzene  
•and hexamethylbenzene, in contact with sulphuric acid:—



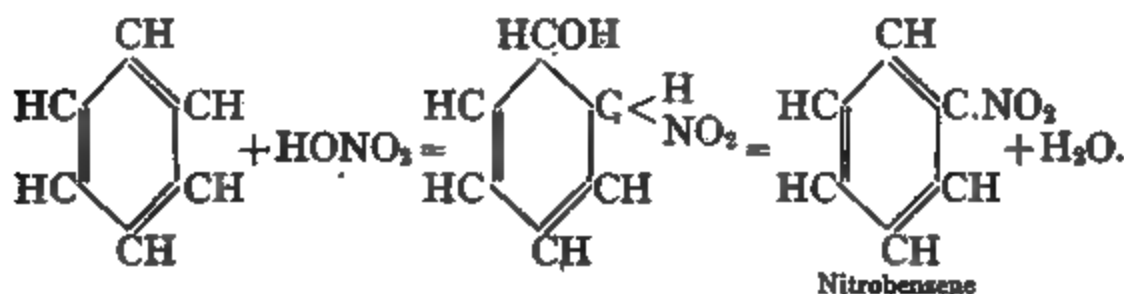
When benzene is treated with chlorine or bromine in the presence of a carrier (iron) it forms *substitution products* and not *addition products*, as might be expected from the above formula. Thus with bromine, bromobenzene and hydrobromic acid are formed:—



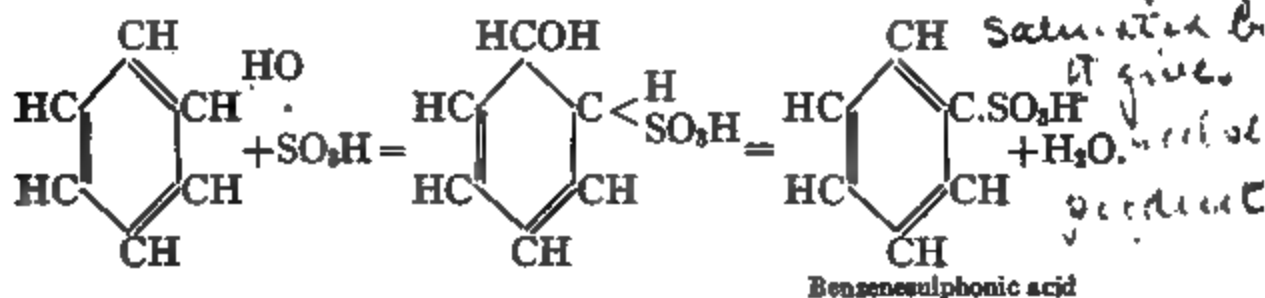
It seems very likely that this apparent contradiction in the chemical conduct of benzene is due to the fact that the hydrocarbon first forms an addition product with bromine and that this then loses hydrobromic acid, reestablishing the double bond:—



This formula for benzene also explains the ease with which benzene and its homologues form nitro compounds with nitric acid and sulphonic acids with sulphuric acid, a fact which distinguishes these hydrocarbons from all the others which have thus far been treated of. Thus, with nitric acid it is probable that an addition product is first formed and that this then loses water to give the nitro compound, reestablishing the double bond:—



With sulphuric acid a similar reaction is assumed to take place.



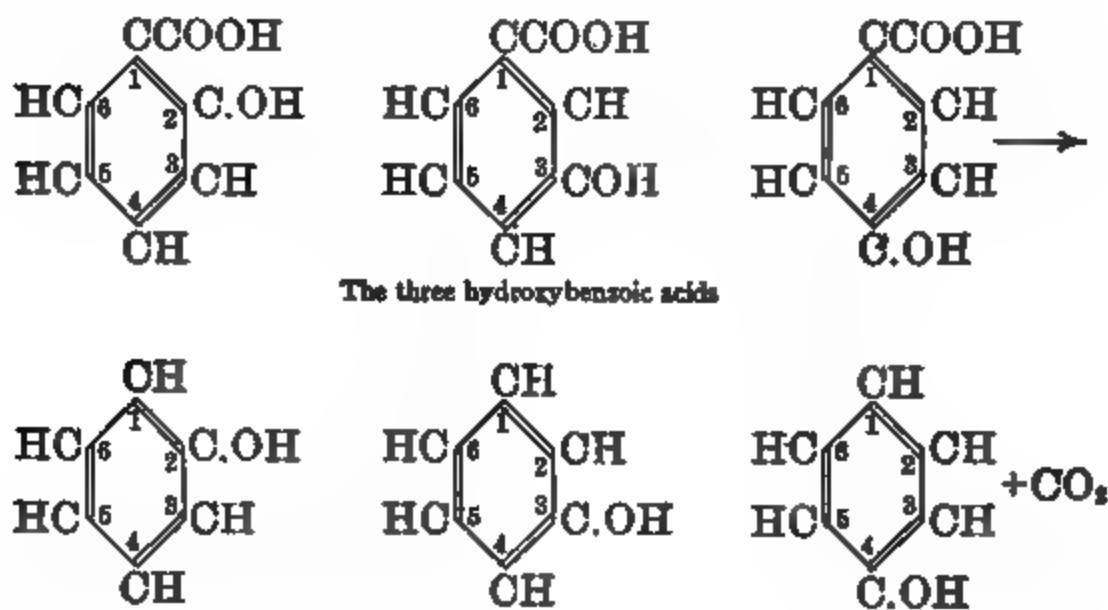
It should be stated that cyclohexane does not form nitro compounds with nitric acid or sulphonic acids with sulphuric acid. It acts like a paraffin hydrocarbon.

The above examples suggest an explanation of the fact that benzene apparently acts as a saturated compound giving substitution products with various reagents.

Benzene combines very readily with ozone, giving a *triozonide*. As it has been shown that a molecule of ozone combines with each double bond of an unsaturated compound (279), it is evident that in this respect benzene acts as though it contains three double bonds.

On the other hand the conclusion cannot be unreservedly drawn that benzene contains three double bonds, certainly not if by double bond is meant an ethylene bond.

The fundamental idea intended to be represented in the Kekulé formula is that benzene is a *symmetrical* compound, that *all the carbon atoms and all the hydrogen atoms bear the same relation to the molecule*. If this formula correctly represents the structure of benzene there should be but one monosubstitution product possible with the same reagent, *i.e.* there should be but one monobromobenzene, one monochlorobenzene, etc. Notwithstanding almost innumerable attempts to make more than one monosubstitution product with the same reagent, no one has yet succeeded. Indeed, it has been shown that it is possible to replace each of the six hydrogen atoms in benzene in turn by the same element (or substituting group) and that the product is always the same. This has been done by starting with ordinary phenol,  $C_6H_5.OH$ , which is hydroxybenzene, and treating it with phosphorus pentabromide. The product is monobromobenzene,  $C_6H_5.Br$ . This can be converted into benzoic acid,  $C_6H_5.COOH$ , by the action of sodium and carbon dioxide. The  $OH$ , the  $Br$ , and the  $COOH$ , therefore, replace the same hydrogen atom (1). There are three isomeric hydroxybenzoic acids,  $C_6H_4.OH.COOH$ , known, all of which can be converted into benzoic acid, and hence the carboxyl group in them also replaces hydrogen (1), while the  $OH$  group must replace other hydrogens in the molecule, say (2), (3), or (4). Each



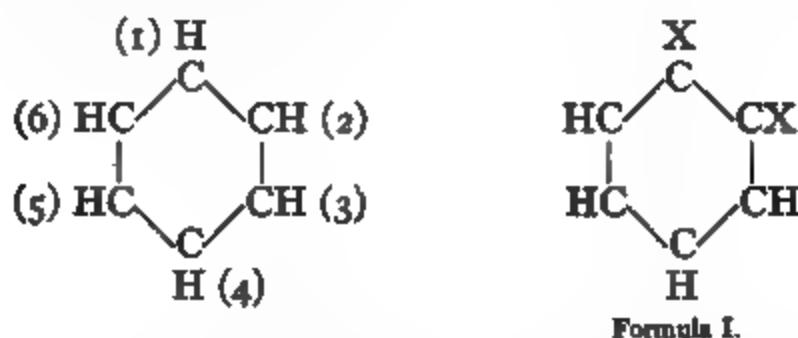
of these three hydroxybenzoic acids gives phenol by splitting off carbon dioxide.

As the hydroxyl group in these three acids occupied the (2), (3), or (4) position, it must occupy these positions in phenol itself. But the phenol obtained in this way is identical with the ordinary phenol with which we started. Hence the four hydrogen atoms (1), (2), (3), and (4) are equivalent.

In a similar manner hydrogen atoms (5) and (6) have been shown to be equivalent to the others. The facts and the theory are in harmony.

The question may fairly be asked, how many disubstitution products does the theory suggest?

Numbering the hydrogens in the formula,<sup>1</sup> we have:—

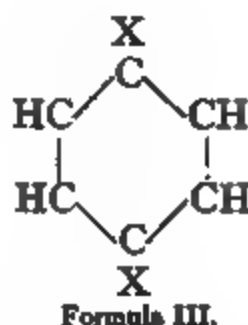
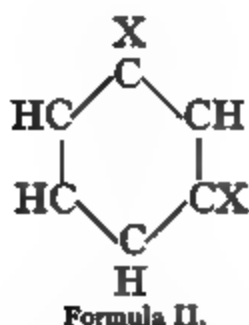


The pairs of hydrogens (1) and (2), (2) and (3), (3) and (4), (4) and (5), (5) and (6), and (6) and (1), bear the same relations to each other and to the molecule; and, according to the formula, whether we replace (1) and (2), or (2) and (3), or (3) and (4), or any other of the above-named pairs, the product ought to be the same. We should get a compound of which Formula I is the general expression, in which X represents any substituting atom or group.

In the second place, the pairs of hydrogens (1) and (3), (2) and (4), (3) and (5), (4) and (6), (5) and (1), and (6) and (2), bear to each other the same relation, but a different relation from that which the above pairs do. Replacing any such pair, we should have a second compound, which is represented by Formula II.

<sup>1</sup>The double bonds are usually omitted for convenience.





Finally, there is a third kind of relation. This is that between the pairs of hydrogens, (1) and (4), (2) and (5), and (3) and (6); and, by replacing such a pair, we should get a compound represented by Formula III above.

The theory suggests no other possibilities. It will thus be seen that the theory indicates the existence of three, and only three, classes of disubstitution products of benzene. There ought to be three, and only three, dichlorobenzenes; three, and only three, dibromobenzenes, etc.

The disubstitution products have been studied very exhaustively for the purpose of determining definitely whether the conclusion above reached is in accordance with the facts; and it may be said at once, that every fact thus far discovered is in harmony with the theory. Three well-defined classes of isomeric disubstitution products of benzene are known, and only three. They are called *ortho*-, *meta*-, and *para*-. In a similar manner it can be shown that three trisubstitution products, three tetra, one penta, and one hexasubstitution product are possible when the substituting element or group is the same. Many examples of these are known. Thus again there is complete agreement between the facts and the theory.

If a model is made representing the Kekulé benzene formula with each carbon atom at the center of a regular tetrahedron, it will be found that all the carbon atoms and all the hydrogen atoms lie in the *same plane*. This is *essential*, for any other space formula that has been proposed for benzene necessitates the existence of optically active isomers, when two of the hydrogen atoms are replaced by dissimilar groups, as in salicylic acid,  $C_6H_4.OH.CO_2H$ . Optically active compounds of this type

have never been prepared nor have they been observed in nature.<sup>1</sup>

The benzene theory has been dealt with somewhat fully, for the reason, that it has played an extremely important part in the study of the benzene derivatives, and that its use serves greatly to simplify the study of these derivatives.

**Toluene,  $C_7H_8$ , ( $C_6H_5.CH_3$ ).** — Toluene was known before it was obtained from coal tar, as it is formed by the dry distillation of Tolu balsam, whence its name. Its relation to benzene is shown by its synthesis from bromobenzene and methyl iodide by the action of sodium: —



Another method for the preparation of toluene and other homologues of benzene consists in treating benzene with a halogen derivative of a paraffin hydrocarbon in the presence of aluminium chloride: —



According to these syntheses, toluene is *methylbenzene*, *i.e.* benzene in which one hydrogen is replaced by methyl; or *phenylmethane*, *i.e.* methane in which one hydrogen atom is replaced by the radical phenyl,  $C_6H_5$ , which bears the same relation to benzene that methyl bears to marsh gas.

Toluene is a colorless liquid that boils at  $110.8^\circ$ ; it has the specific gravity 0.8812 at  $4^\circ$  compared with water at  $4^\circ$ ; and has a pleasant aromatic odor.

It is very susceptible to the action of reagents, yielding a large number of substitution products, some of the most important of which will be taken up later.

But one toluene or methylbenzene has ever been discovered.

It takes up hydrogen and gives methylcyclohexane when its vapor mixed with hydrogen is passed over finely divided nickel heated to  $180^\circ$ .

Towards oxidizing agents its conduct is peculiar and interesting. The methyl is oxidized, while the phenyl remains

<sup>1</sup> See *Stereochemistry* by A. W. Stewart, 2d ed., 1919, page 216.

intact. The product is the well-known acid, benzoic acid, which, as we have seen, breaks down readily into carbon dioxide and benzene. It has the composition  $C_7H_6O_2$ , and is the carboxyl derivative of benzene,  $C_6H_5.CO_2H$ . The oxidation of toluene is represented by the equation:—



Refined toluene to the extent of 2,740,000 gallons was produced // in the United States in 1920.

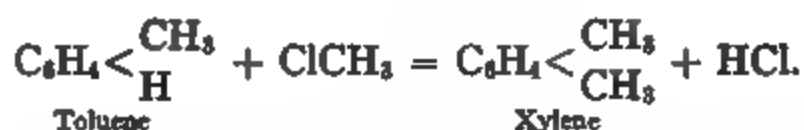
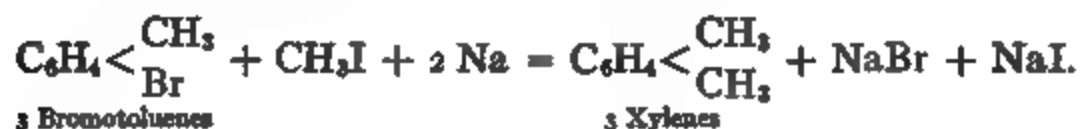
**Xylenes,  $C_8H_{10}$  [ $C_6H_4(CH_3)_2$ ].**—That portion of light oil which boils at about  $140^\circ$  was originally called *xylene*. It was afterwards found that this xylene consists of three isomeric hydrocarbons (91–93.5 per cent meta, 4.8–8.1 per cent ortho, and about 1.7 per cent para). As the boiling points of these three substances lie near together, it is difficult to separate them by means of fractional distillation. By treatment with sulphuric acid the ortho and metaxylene dissolve (forming sulphonic acids), while the para does not. The para product is then drawn off and the ortho and metasulphonic acids are separated from each other by fractional crystallization of their sodium salts. The xylenes are regenerated from their sulphonic acids by superheating with water. They are known as *orthoxylene*, *metaxylene*, and *paraxylene*.

*Orthoxylene* boils at  $144.4^\circ$ .

*Metaxylene* boils at  $139.2^\circ$ .

*Paraxylene* boils at  $138.2^\circ$ .

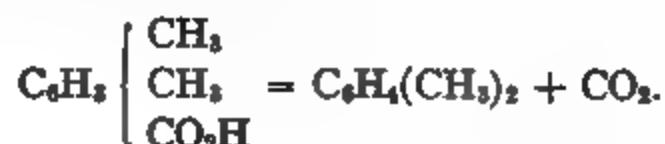
These hydrocarbons have also been obtained from toluene by means of the reactions made use of for the purpose of converting benzene into toluene:—



This shows that they are all *methyltoluenes*. There are three monobromotoluenes, known as ortho, meta, and para

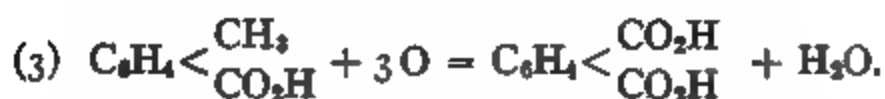
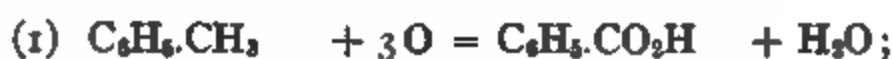
bromotoluene. For the preparation of orthoxylylene, ortho-bromotoluene is used; metabromotoluene yields metaxylylene, and parabromotoluene yields paraxylylene.

Ortho, meta, and paraxylylene have also been obtained from certain acids, which bear to them the same relation that benzoic acid bears to benzene:—



The reaction by which *metaxylylene* is formed from *mesitylenic acid* is of special importance in determining its structure, as will be pointed out (325).

On oxidation, the xylenes undergo changes like that which is illustrated in the formation of benzoic acid from toluene, consisting in the oxidation of methyl to carboxyl. The first change gives monobasic acids, one corresponding to each xylene. By further oxidation, these three monobasic acids are converted into dibasic acids. Thus, we have the three reactions, all of the same kind:—

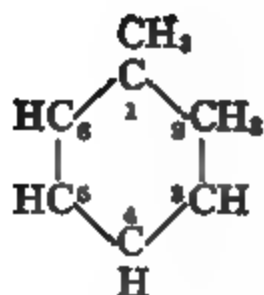


The three monobasic acids of the formula  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ < \\ \text{CO}_2\text{H} \end{smallmatrix}$  are known as *orthotoluic*, *metatoluic*, and *paratoluic* acids, respectively; and the three dibasic acids obtained from them are known as *orthophthalic*, *metaphthalic*, and *paraphthalic* acids. Starting thus with the three bromotoluenes, we get, first, three xylenes, then three toluic acids, and finally three phthalic acids. In each case, we distinguish between the three isomeric compounds by the prefixes *ortho*, *meta*, and *para*. In a similar way, all disubstitution products of benzene are designated. We therefore have three series into which all

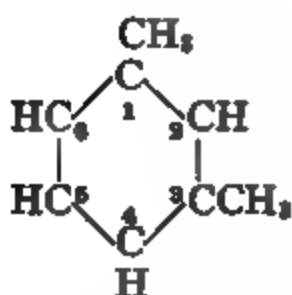
disubstitution products of benzene can be arranged; and these are known as the *Ortho series*, the *Meta series*, and the *Para series*. In arranging them in this way, we may select any prominent disubstitution product, and call it an *ortho compound*; and then call one of its isomers a *meta compound*, and the other a *para compound*. Having thus a representative of each of the three classes, the remainder of the problem consists in determining for each disubstitution product, by means of appropriate reactions, into which one of the three representatives it can be transformed. If from a given compound we get the representative of the ortho series, we conclude that the compound belongs to the ortho series; if we get the representative of the meta series, we conclude that the compound is a meta compound; and if we get the representative of the para series, we conclude that the compound is a para compound. As representatives, we may select either the three xylenes or the three phthalic acids.

This classification of the disubstitution products of benzene into the ortho, meta, and para series, by means of chemical transformations, is entirely independent of any hypothesis regarding the nature of benzene. We may now ask, however, which one of the three general expressions given above (see formulas I, II, and III, 315, 316) represents the relation of the groups in the ortho compounds; which one the relation in the meta compounds; and which one the relation in the para compounds. If we can answer these questions for any three isomeric disubstitution products of benzene, the answer for the rest will follow. To reduce the problem to simple terms, therefore, let us take the three xylenes. There are three xylenes and three formulas; is it possible to determine which particular formula to assign to each xylene?

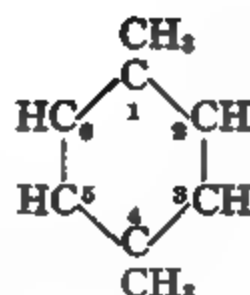
As may be imagined, this determination is by no means a simple matter; and it has been the occasion of a great many investigations. Theoretically, the simplest method available consists in carefully studying the substitution products of each xylene, to discover how many varieties of monosubstitution products can be obtained from each. The formulas are: —



Formula I.



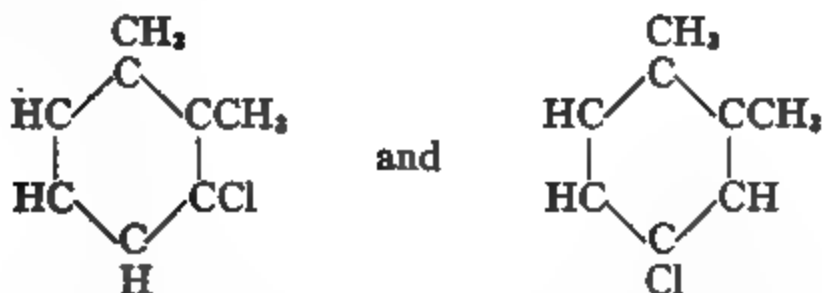
Formula II.



Formula III.

Each of the four benzene hydrogens of the xylene of formula III bears the same relation to the molecule. It therefore should make no difference which one is replaced by bromine, the product ought to be the same. This is not true of the xylenes represented by formulas I and II. That xylene, whose structure is represented by formula III, ought, therefore, to yield but one monosubstitution product with bromine. On studying the xylenes, we find the one which boils at  $138.2^\circ$ , called paraxylene, yields but one monosubstitution product; that is, we can get from it only one monobromoxylene; only one mononitroxylene, etc. We therefore conclude that paraxylene is represented by formula III above; and, further, the formula III, on p. 316, is the general expression for all para compounds, as they can all be made from paraxylene or be converted into paraxylene.

Examining formula I in the same way, we see that H(3) and H(6) bear the same relation to the molecule; and that H(4) and H(5) also bear the same relation to the molecule, though different from that of H(3) and H(6). Two chloroxylenes of the formulas



ought to be obtainable from the xylene of formula I.

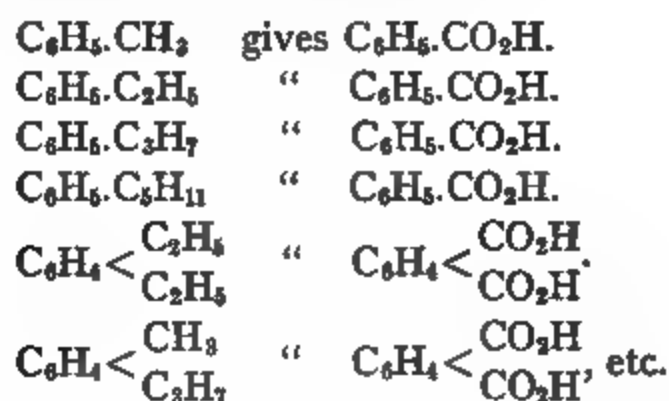
In the same way three chloroxylenes should be obtainable from the xylene of formula II. The method, the principle

of which is thus indicated briefly, while theoretically simple enough, is very difficult in its application, except in the case of the para compound. Other methods have therefore been used, and these will be discussed under mesitylene, naphthalene, and phthalic acid. It may be said, in anticipation, that the result of all observations points to formula I for ortho-xylene, to formula II for metaxylene, and to formula III for paraxylene.

**Ethylbenzene**,  $C_8H_{10}(C_6H_5.C_2H_5)$ . This hydrocarbon is isomeric with the xylenes, but differs from them in containing an ethyl group in the place of one hydrogen of benzene, instead of two methyl groups in the place of two hydrogens of benzene. It boils at  $136.5^\circ$ . It is made by treating a mixture of bromobenzene and ethyl bromide with sodium:—



Its conduct towards oxidizing agents distinguishes it from the xylenes. It yields benzoic acid, just as toluene does. In this case, as in that of toluene, the paraffin radical is oxidized to carboxyl. It has been found that no matter what this radical is, it is oxidized to carboxyl, carbon dioxide, and water. Thus, the conversions indicated below take place:—



**Mesitylene**,  $C_9H_{12}[C_6H_3(CH_3)_3]$ . Mesitylene is contained in small quantity in light oil, and can be obtained in pure condition from this source. It is most readily prepared by treating acetone with sulphuric acid:—

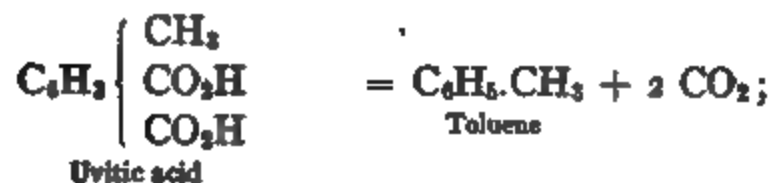
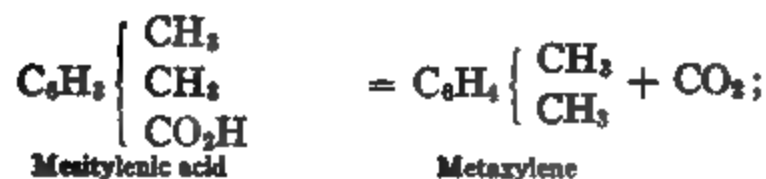
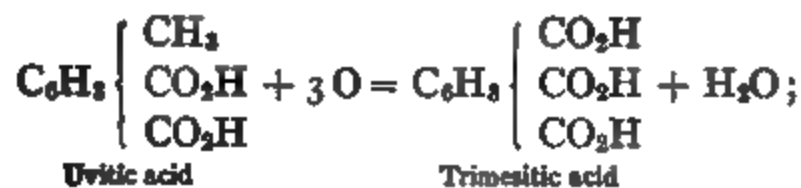
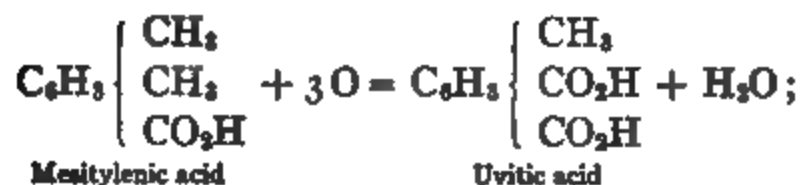
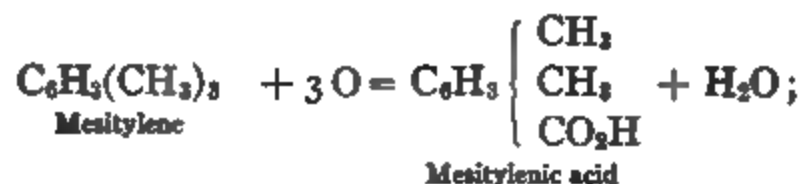


It can also be made by treating methylacetylene,  $\text{CH}_3\text{C}\equiv\text{CH}$ , with sulphuric acid, the action in this case being perfectly analogous to the polymerization of acetylene (311):—



It is a liquid resembling the lower members of the series in its general properties. It boils at  $165^\circ$ .

Its conduct towards oxidizing agents shows that it is a *trimethylbenzene*. When boiled with dilute nitric acid, it yields *mesitylenic acid*,  $\text{C}_9\text{H}_{10}\text{O}_2$ , and *uvitic acid*,  $\text{C}_9\text{H}_8\text{O}_4$ ; and, by further oxidation, *trimesitic acid*,  $\text{C}_9\text{H}_6\text{O}_6$ , is formed. By distillation with lime, mesitylenic acid yields metaxylene and carbon dioxide; uvitic acid yields toluene and carbon dioxide; and trimesitic acid yields benzene and carbon dioxide. The formation and decomposition of the acids are represented by the equations following:—







These transformations show clearly that mesitylene is trimethylbenzene, but they do not show in what relation the three methyl groups stand to each other.

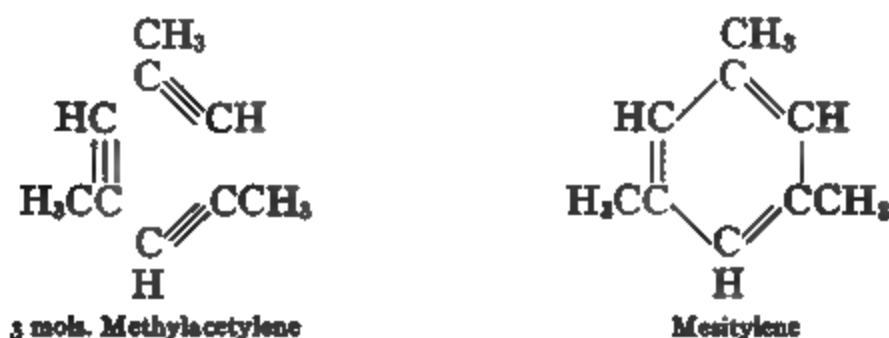
An ingenious speculation in regard to this relation is based upon the fact that mesitylene is formed from acetone. It appears probable that each of the three molecules of acetone taking part in the reaction,



undergoes the same change. As the product contains three methyl groups, the simplest assumption that can be made is that each acetone molecule gives up water as represented thus:—



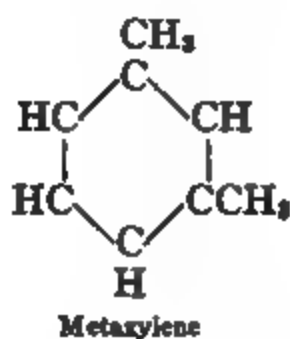
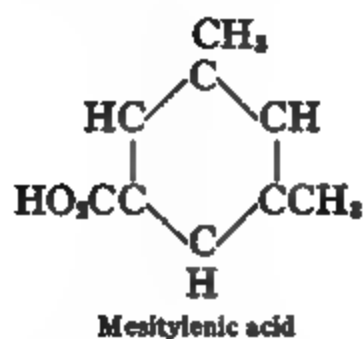
We thus have three molecules of methylacetylene,  $\text{CH}_3\text{—C}\equiv\text{CH}$ , and these unite to form trimethylbenzene. The only way in which the union can be represented, assuming that all three act in the same way, is this:—



According to this, mesitylene is a symmetrical compound,—that is to say, each of the three methyl groups bears the same relation to the molecule; and the same is true of each of the three benzene hydrogen atoms.

This view has been tested by substituting bromine for the

three hydrogen atoms of the benzene residue successively; and it has been found to be correct, as but one monobromine substitution product of mesitylene has ever been obtained. Accepting the formula above given for mesitylene, an important conclusion follows regarding the structure of metaxylene. For we have seen that, by oxidizing mesitylene, we get, as the first product, mesitylenic acid, — which is mesitylene, one of whose methyls has been oxidized to carboxyl. As all the methyl groups bear the same relation to the molecule, it makes no difference which one is oxidized. The acid has the formula: —

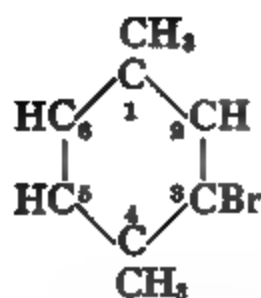


Now, by distilling this acid with lime, carbon dioxide is given off, and metaxylene is produced.

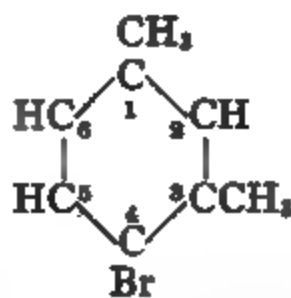
As the change consists in replacing the carboxyl by hydrogen, it follows that metaxylene must be represented by the above formula, and consequently that, in all meta compounds, the two substituting atoms or groups bear to each other the relation which the two methyl groups bear to each other in this formula for metaxylene.

**Pseudocumene**,  $\text{C}_9\text{H}_{12}[\text{C}_6\text{H}_3(\text{CH}_3)_3]$ . — This hydrocarbon, which is isomeric with mesitylene, occurs in light oil, from which it can be prepared in pure condition. Its properties are similar to those of the lower members of the series. It boils at  $169.5^\circ$ .

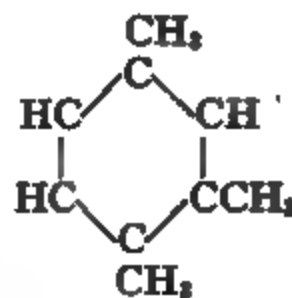
Pseudocumene has been made synthetically from 3-bromoparaxylene and methyl iodide, and also from 4-bromometaxylene and methyl iodide by heating with sodium. How this is possible will be understood by an examination of the formulas on the next page: —



3-Bromoparaxylene



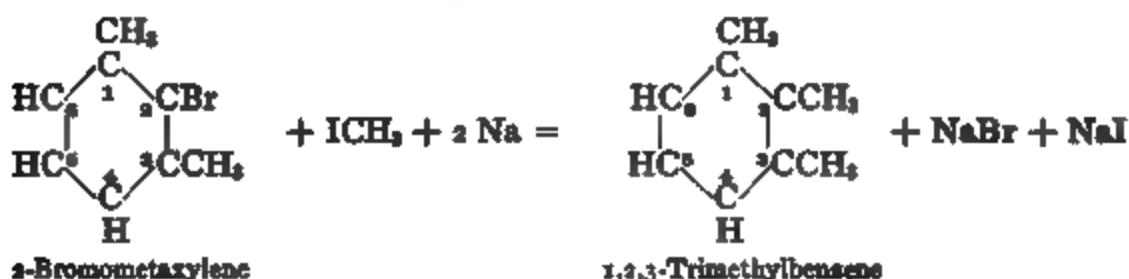
4-Bromometaxylene



Pseudocumene

Replacing the bromine by methyl, in either of the compounds represented, the product would have the same formula, which is that of pseudocumene, or 1,3,4-trimethylbenzene.

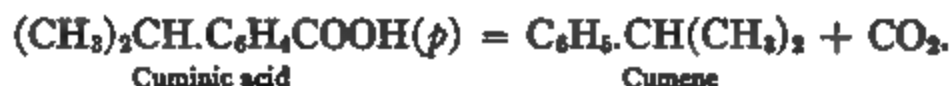
**Hemimellitene** is 1,2,3-trimethylbenzene. It occurs in light oil. It has been made from 2-bromometaxylene, methyl iodide, and sodium:—



It boils at 175°.

Mesitylene, 1,3,5-trimethylbenzene, is also called symmetrical trimethylbenzene or *s*-trimethylbenzene; pseudocumene, 1,3,4-trimethylbenzene, unsymmetrical trimethylbenzene or *u*-trimethylbenzene; and hemimellitene, 1,2,3-trimethylbenzene, vicinal trimethylbenzene or *v*-trimethylbenzene. Similarly, other trisubstitution products of benzene are designated as *s*, *u*, and *v*.

**Cumene**, isopropylbenzene,  $C_6H_5.CH(CH_3)_2$ , is obtained from cuminic acid (*p*-isopropylbenzoic acid) by distillation with lime:—



It is isomeric with the trimethylbenzenes and has been made from bromobenzene, isopropyl bromide, and sodium:—



It has a pleasant odor and boils at  $152.9^{\circ}$ . On oxidation it gives benzoic acid.

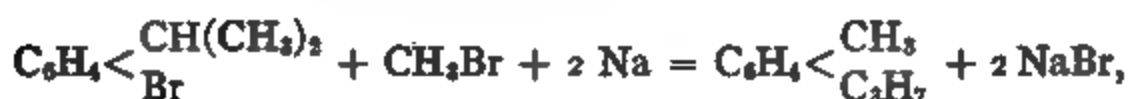
*p*-Cymene, paramethylisopropylbenzene,  $C_{10}H_{14} \left( C_6H_4 < \begin{smallmatrix} CH_3 \\ C_3H_7 \end{smallmatrix} \right)$ . —

This hydrocarbon is of special importance, on account of its close connection with two well-known groups of natural substances, — the groups of which camphor and the terpenes are the best known representatives. It occurs in the oil of caraway, the oil of thyme, and in the oil of eucalyptus. The terpenes are hydrocarbons of the formula  $C_{10}H_{16}$ , of which oil of turpentine is the best-known. This substance easily gives up two hydrogen atoms and yields *p*-cymene when heated with iodine. *p*-Cymene is best prepared by heating camphor with phosphorus pentoxide: —



It is a liquid of a pleasant odor. It boils at  $176.5^{\circ}$ .

It has been made synthetically from parabromoisopropylbenzene and methyl bromide: —



which clearly shows its relation to benzene. When oxidized it gives *p*-toluic and *p*-phthalic acids: —



*p*-Cymene is the chief constituent of spruce turpentine, a by-product of the manufacture of sulphite pulp.

**Metacymene, meta-methylisopropylbenzene,**  $C_{10}H_{14} < \begin{smallmatrix} CH_3 \\ C_3H_7(m) \end{smallmatrix}$ .

—This has been found in the products of distillation of rosin (rosin spirits).

**Tertiary butyl-*m*-xylene,**  $H_3C \begin{array}{c} CH_3 \\ | \\ \text{C}_6H_4 \\ | \\ C(CH_3)_3 \end{array}$  is made by

treating *m*-xylene with isobutyl chloride in the presence of

aluminium chloride. It is made on the large scale by this method and used in the preparation of "artificial musk" (341).

### HYDROAROMATIC HYDROCARBONS

Russian petroleum, like American petroleum, consists very largely (80 per cent) of saturated hydrocarbons (10 per cent aromatic hydrocarbons), but, while most of the American petroleum consist of paraffins, Russian petroleum is made up of saturated cyclic hydrocarbons, hexahydro addition products of the aromatic hydrocarbons, having the general formula,  $C_nH_{2n}$  and called *naphthenes*. They are isomeric with the olefines, but differ from them in being saturated. They do not form addition products with bromine and, unlike the aromatic hydrocarbons, do not form nitro compounds with nitric acid or sulphonic acids with sulphuric acid. They are readily converted into the aromatic hydrocarbons by the loss of hydrogen and have been made from the benzene hydrocarbons by the addition of hydrogen.

Cyclohexane, hexamethylene,  $H_2C \begin{array}{c} H_2C \quad CH_2 \\ \diagup \quad \diagdown \\ CH_2 \quad CH_2 \\ \diagdown \quad \diagup \\ H_2C \quad CH_2 \end{array} CH_2$ , has been found

in American, Rumanian, Galician, and especially in Russian petroleum. It has been made by reducing iodocyclohexane and also from 1, 6-dibromohexane by abstracting bromine with sodium (305).

It is most readily obtained by reducing benzene by passing its vapor mixed with hydrogen over finely divided nickel heated to  $180^\circ$ . It was made in this way during the World War and used in airplane engines. It boils at  $80.85^\circ$  and melts at  $4.7^\circ$ . Chlorine and bromine give substitution products. In its chemical conduct it resembles hexane closely, hence the name cyclohexane. The higher members of this series of hydrocarbons are homologues of cyclohexane and are made by the reduction of the homologues of benzene. Thus, hexahydrotoluene and the hexahydroxylenes are methyl and dimethyl derivatives of cyclohexane. They are present in Russian petroleum.

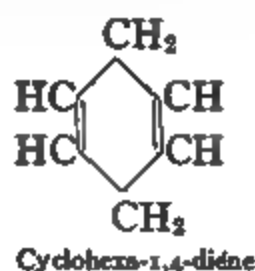
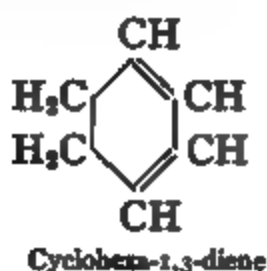
**Hexahydro-*p*-cymene, menthane, terpane,  $C_{10}H_{20}$** , is especially important on account of its relation to the terpenes and camphors. It will be taken up in connection with these substances.

**Cyclohexene, tetrahydrobenzene,**  $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH} \\ | \qquad \qquad || \\ \text{CH}_2-\text{CH}_2-\text{CH} \end{array}$ , is made

from bromocyclohexane by abstracting hydrobromic acid with alcoholic caustic potash. It boils at  $82.3^\circ$  and acts like the olefines, forming a dibromide with bromine. Tetrahydrotoluene and tetrahydroxylenes, which are methyl and dimethyl derivatives of cyclohexene and resemble this substance very closely in their chemical conduct, are also known. Tetrahydrotoluene occurs in rosin spirits.

**Tetrahydrocymene,  $C_{10}H_{18}$** , is a homologue of tetrahydrobenzene and is related to the terpenes (441).

**Dihydrobenzenes,  $C_6H_8$** , have been obtained from the two dibromocyclohexanes by abstracting hydrobromic acid with alcoholic caustic potash. Two isomers are known, which resemble each other very closely in their properties.

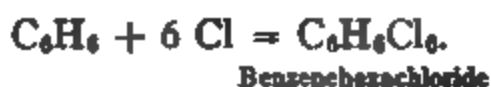


They combine with two and four atoms of bromine, decolorize a solution of potassium permanganate and resemble the olefines in their properties.

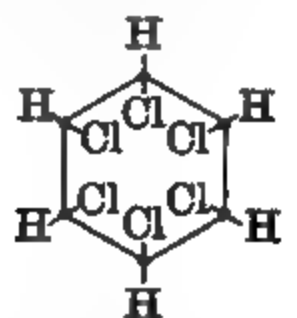
**Dihydro-*o*-xylene** is called cantharene, as it has been obtained by distilling cantharic acid with lime.

#### ACTION OF HALOGENS ON BENZENE. ADDITION PRODUCTS

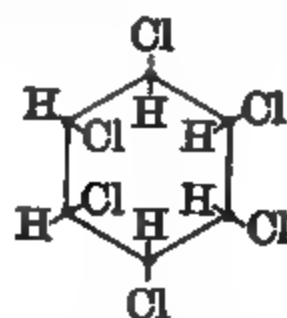
When chlorine or bromine acts on benzene, addition products are formed:—



This reaction is much facilitated by the action of sunlight. Hexahalogen addition products are also formed when the halogens act on benzene at the boiling point or, in the cold, in the presence of a solution of sodium hydroxide. They are hexahalogen substitution products of cyclohexane, and the two stereoisomers required by the Kekulé formula are both formed:—



Cis-benzenehexachloride



Trans-benzenehexachloride

The one in which all the hydrogen atoms are on one side of the plane passing through the carbon atoms (the plane of the paper) and all the halogen atoms on the opposite side is known as the *cis* form. The other, in which four hydrogen atoms and two halogens are on one side and four halogens and two hydrogens on the other, is known as the *trans* form. Both forms of the benzene hexachloride are decomposed by alcoholic caustic potash, giving the unsymmetrical trichlorobenzene:—



That is, the isomerism disappears when the benzene condition is reestablished.

Benzene also combines, in the dark and at  $0^\circ$ , with chlorine monoxide to give the two benzene hexachlorides, and with hypochlorous acid to give benzene trichlorohydrin:—



#### HALOGEN SUBSTITUTION PRODUCTS OF BENZENE

Chlorine also acts on benzene to give substitution products (312):—



The reaction is slow and incomplete, however, unless a catalyst (iodine, iron, etc.) is present. The iodine and iron first form chlorides, which then give up chlorine to the benzene and are regenerated by the action of more chlorine. They hence act as *chlorine carriers*. Thus, monochlorobenzene has been made by heating benzene with ferric chloride: —



Most of the elements (I, S, P, Sb, Mo, Sn, Tl) which act as chlorine carriers, like iron, form two chlorides. The exception to this rule is aluminium chloride, which is an excellent chlorine carrier.

By the further action of chlorine on benzene or on monochlorobenzene, in the presence of a *catalyst*, *para*-dichlorobenzene is the main product of the reaction, smaller amounts of the *ortho* and *meta* products being formed at the same time. The proportion of the isomers formed is influenced by the nature of the catalyst. Thus, in the presence of aluminium chloride 65.7 per cent of *para*, 29.6 per cent *ortho*, and 4.7 per cent *meta*-dichlorobenzene are formed, while with ferric chloride as a catalyst the percentages are 55.5, 39.2, and 5.3. Further chlorination gives mainly the *unsymmetrical* trichlorobenzene, as this product results from the chlorination of all three of the dichlorobenzenes. It has already been stated that this trichlorobenzene is the only product resulting from the abstraction of hydrochloric acid from the two benzene hexachlorides with alcoholic caustic potash. The tetrachlorobenzene, which results from the further chlorination, is the symmetrical product, 1,2,4,5, and this is then converted into pentachloro and hexachlorobenzene ( $\text{C}_6\text{Cl}_6$ ) by more energetic chlorination.

The chlorine substitution products of benzene differ markedly from those of the marsh gas series in that the chlorine can only be replaced with great difficulty. Thus it is not possible to replace the chlorine by hydroxyl by heating with alkali or by an amino group with ammonia, except by heating to a high temperature in an autoclave, and then the reaction is



incomplete. By heating with sodium and alcohol, however, reverse substitution takes place and the hydrocarbon is regenerated: —



**Monochlorobenzene**,  $\text{C}_6\text{H}_5\text{Cl}$ , is made on the large scale by chlorinating benzene in the presence of iron. The three dichlorobenzenes are always formed in this reaction as by-products (see above), even when a large excess of benzene is used. The monochlorobenzene is separated from them and from the excess of benzene by distillation. Chlorobenzene can also be made by the action of phosphorus pentachloride on hydroxybenzene (phenol): —



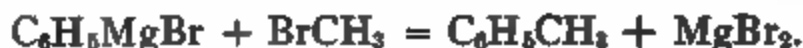
but the reaction does not take place as readily as in the case of alcohols, and it is simpler and more economical to make it by the chlorination of benzene. Chlorobenzene also results from the decomposition of benzene diazonium chloride (353) by cuprous chloride or copper powder: —



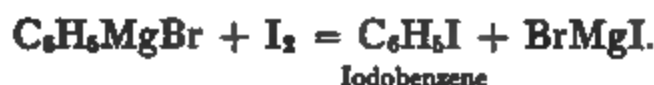
Chlorobenzene is a colorless liquid, having a pleasant odor. It boils at  $132^\circ$  and melts at  $-45^\circ$ . It is used in large quantities in the manufacture of sulphur dyes and in the preparation of chloronitrobenzenes and other dyestuff intermediates. During the World War picric acid (378) was made from chlorobenzene. Nearly 5,000,000 pounds were produced in 1920 in the United States.

**Bromobenzene**,  $\text{C}_6\text{H}_5\text{Br}$ . — This is made by the same methods as those used in making chlorobenzene. It boils at  $157^\circ$  and melts at  $-31^\circ$ .

When bromobenzene in solution in ether is treated with magnesium powder, it forms phenyl magnesium bromide,  $\text{C}_6\text{H}_5\text{MgBr}$ . (See Grignard reaction (112).) This reacts with methyl bromide to form methylbenzene or toluene, thus: —



Phenyl magnesium bromide is much used in synthetical work for the purpose of introducing the phenyl group. Thus, in the reaction above, the phenyl group is introduced into methane. This reagent is also used for the purpose of substituting iodine for bromine: —



The bromine can also be removed from bromobenzene by sodium (317) and by nascent hydrogen.

**Iodobenzene,  $\text{C}_6\text{H}_5\text{I}$ .** — This can be made by heating benzene with iodine and iodic acid in a sealed tube: —



but it is more easily made from the diazonium salt: —



It is a liquid that boils at  $188^\circ$ , and melts at  $-30^\circ$ .

**Iodobenzene dichloride,  $\text{C}_6\text{H}_5\text{ICl}_2$ .** — This compound is formed when iodobenzene in chloroform solution is treated with chlorine. When it is treated with a solution of caustic potash, it is converted into iodosobenzene,  $\text{C}_6\text{H}_5\text{IO}$ . This has basic properties, and forms salts that are derived from the hypothetical base,  $\text{C}_6\text{H}_5\text{I}(\text{OH})_2$ , as, for example, the iodobenzene dichloride given above.

**Iodoxybenzene,  $\text{C}_6\text{H}_5\text{IO}_2$ ,** is formed from iodosobenzene, either by heating it alone or by boiling its water solution: —



**Diphenyliodonium hydroxide,  $(\text{C}_6\text{H}_5)_2\text{I.OH}$ .** — This remarkable substance is formed when a mixture of iodoso and iodoxybenzene is shaken with silver oxide and water: —



It is a strongly alkaline base and forms salts that have many points of resemblance with the thalious salts. It is known only in solution.

Diphenyliodonium hydroxide may be regarded as the diphenyl derivative of a hypothetical base, iodonium hydroxide,  $\text{H}_2\text{I}(\text{OH})$ , that bears to iodine a relation similar to that which ammonium hydroxide bears to nitrogen. Similar compounds of sulphur are known in which sulphur plays the same part that iodine plays in the iodonium compounds, and nitrogen in the ammonium compounds, such as trimethylsulphonium hydroxide  $(\text{CH}_3)_3\text{S.OH}$ .

Dibromobenzene,  $\text{C}_6\text{H}_4\text{Br}_2$ , is one of the products of the direct treatment of benzene with bromine in the presence of a carrier. This being a disubstitution product of benzene, it follows, from what has been said in regard to isomerism in this series of hydrocarbons, that three isomeric varieties of the substance ought to be obtainable; and the interesting question suggests itself: Which one of the three possible dibromobenzenes is formed by direct treatment of benzene with bromine? The answer to the question is equally interesting. The main product of the action is *para*-dibromobenzene, while there are always formed in smaller quantity some of the *ortho* product and some of the *meta* product.

In studying the disubstitution products of benzene, one of the first problems that presents itself is the determination of the relations which the substituting atoms or groups bear to each other. The determination is made by transforming the compounds into others, the relations of whose groups are known. Thus, to illustrate, when benzene is treated under the proper conditions with bromine, three dibromobenzenes are formed. Without investigation, we, of course, cannot tell to which series these compounds belong. But, by treating that product which is formed in *largest* quantity with methyl iodide and sodium, we get *paraxylene*. In other words, by replacing the two bromine atoms of the dibromobenzene by methyl groups, we get a compound which we know belongs to the *para* series; and, therefore, we have determined that this bromine product is a *para* compound. In a similar manner the dibromobenzenes formed in smaller quantity can be converted into *o*-xylene and into *m*-xylene.

## HALOGEN DERIVATIVES OF TOLUENE

As toluene contains a residue of marsh gas, methyl,  $\text{CH}_3$ , and a residue of benzene, phenyl,  $\text{C}_6\text{H}_5$ , it yields two classes of substitution products: (1) Those in which the substituting atom or group replaces one or more hydrogen atoms of the phenyl group; and (2) those in which the substitution takes place in the methyl. In general, when treated with chlorine or bromine in direct sunlight, or at the boiling temperature, toluene yields products of the second class; while, in the presence of iodine or some other carrier (331), it yields products of the first class. Thus, we have the two parallel series of chlorine derivatives:—

## I

Monochlorotoluene,	$\text{C}_6\text{H}_4\text{Cl}.\text{CH}_3$
Dichlorotoluene,	$\text{C}_6\text{H}_3\text{Cl}_2.\text{CH}_3$
Trichlorotoluene,	$\text{C}_6\text{H}_2\text{Cl}_3.\text{CH}_3$

## II

Benzyl chloride,	$\text{C}_6\text{H}_5.\text{CH}_2\text{Cl}$
Benzal chloride,	$\text{C}_6\text{H}_5.\text{CHCl}_2$
Benzotrichloride,	$\text{C}_6\text{H}_5.\text{CCl}_3$

When a member of the first class is oxidized, the methyl is oxidized to carboxyl and the rest of the compound remains unchanged, as in the case of toluene. Thus, the first substance of class I yields  $\text{C}_6\text{H}_4\text{Cl}.\text{CO}_2\text{H}$ ; the second,  $\text{C}_6\text{H}_3\text{Cl}_2.\text{CO}_2\text{H}$ , etc. These products are *monochloro* and *dichlorobenzoic acids*. On the other hand, all the members of the second class yield the same product that toluene does; viz., *benzoic acid*. Hence, by treatment with oxidizing agents, it is easy to distinguish between the members of the two classes. Further, the halogen atoms contained in the methyl react like the halogen atoms in paraffin derivatives, while those in the phenyl do not. When, for example, benzal chloride,  $\text{C}_6\text{H}_5.\text{CHCl}_2$ , is superheated with water, both chlorine atoms are replaced by oxygen, the product being the aldehyde  $\text{C}_6\text{H}_5.\text{CHO}$ , *oil of bitter almonds*, just as ordinary

aldehyde is formed from ethylidene chloride (48) by the action of water. When, however, the isomeric *dichlorotoluene* is superheated with water, no change takes place.

Regarding those simple substitution products of toluene which contain one halogen atom in the phenyl, such as monochloro and monobromotoluene,  $C_6H_4Br.CH_3$ , it will be seen that they are disubstitution products of benzene, and hence capable of existing in three isomeric varieties, ortho, meta, and para. The products formed by direct treatment of toluene with chlorine or bromine are mixtures of about equal parts of the para and the ortho compounds.

The determination of the series to which each of these products belongs can be made by replacing the halogen by methyl, and thus getting the corresponding xylene. One product of the action of bromine on toluene is in this way converted into paraxylene, and is therefore parabromotoluene. In a similar way the second product gives orthoxylene and hence is orthobromotoluene.

All the members of the first class resemble very closely the chlorine substitution products of benzene, of which they are homologues.

**Benzyl chloride**,  $C_6H_5CH_2Cl$ , and **benzyl bromide**,  $C_6H_5CH_2Br$ , are made by chlorinating or brominating toluene at the boiling point. The chloride boils at  $178^\circ$  and the bromide at  $198^\circ$ . The iodide,  $C_6H_5CH_2I$ , can be made from the bromide by heating this with a solution of potassium iodide. These compounds are esters of benzyl alcohol (phenylmethyl alcohol),  $C_6H_5CH_2OH$ , and they are converted into this alcohol by boiling with potassium carbonate solution. The chlorine in the side chain is easily replaced. Thus, by heating benzyl chloride with potassium acetate, benzyl acetate is formed; with sodium hydrosulphide, benzylmercaptan; and with ammonia, benzylamine. Toluene derivatives with the halogen in the side chain have an exceedingly irritating effect on the mucous membrane of the eyes and nose, causing the secretion of tears. Benzyl iodide was one of the "tear gases" used during the World War.

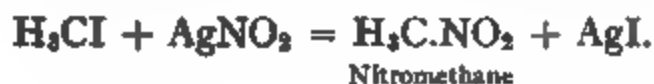
**Benzal chloride**,  $C_6H_5CHCl_2$ , and **benzotrichloride**,  $C_6H_5CCl_3$ , are made by further chlorination of toluene at the boiling point. Like benzyl chloride, these chlorides are made on the large scale and are very important substances. Benzyl chloride is used in making benzyl alcohol, and also in the manufacture of certain dyes. Benzal chloride is used in making benzaldehyde and as a synthetical reagent. Benzotrichloride is used in the manufacture of benzoic acid on the large scale.

#### HALOGEN DERIVATIVES OF THE HIGHER MEMBERS OF THE BENZENE SERIES

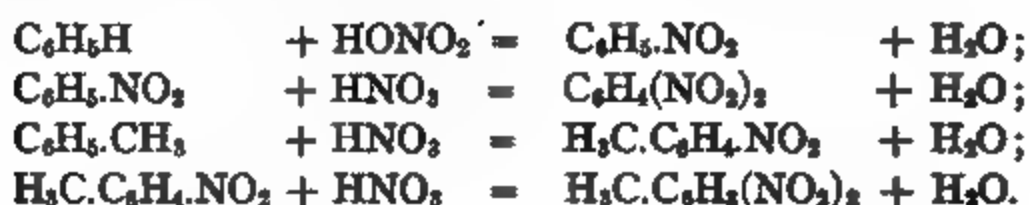
Concerning the halogen derivatives of the xylenes it need only be said that the only one of the three xylenes from which pure products can easily be obtained is paraxylene. When this is treated with bromine, it yields but one monobromoxylene. The significance of this fact has been discussed above. The monosubstitution products obtained from the other xylenes are mixtures which it is very difficult, and in some cases impossible, to separate into their constituents. Mesitylene and pseudocumene, though both are trimethylbenzenes, conduct themselves quite differently towards bromine, — the former yielding only one monobromine substitution product; the latter, a mixture of several.

#### NITRO COMPOUNDS OF BENZENE AND TOLUENE

In treating of nitro compounds in connection with the paraffin derivatives (107), it was stated that they are obtained much more readily from the benzene hydrocarbons than from the paraffins. Only a few nitro derivatives of the paraffins are known. As will be remembered, they cannot readily be prepared by treating the paraffins with nitric acid, but must be made by circuitous methods, the principal one being the treatment of the halogen derivatives with silver nitrite: —



The preparation of a nitro derivative of a hydrocarbon of the benzene series is a simple matter. It is only necessary to bring the hydrocarbon in contact with fuming nitric acid, or better with a mixture of sulphuric and nitric acids, when reaction takes place, and one or more hydrogen atoms of the hydrocarbon are replaced by the nitro group,  $\text{NO}_2$ , as represented in the equations:—



The nitro compounds thus obtained are not acids, nor are they esters of nitrous acid. If they were esters of nitrous acid, they would be saponified by caustic alkalies, yielding a nitrite and a hydroxyl derivative similar to the alcohols. They do not act in this way. When treated with nascent hydrogen, they are reduced to amino compounds or substituted ammonias. Thus, nitrobenzene,  $\text{C}_6\text{H}_5\text{NO}_2$ , gives aniline or aminobenzene,  $\text{C}_6\text{H}_5\text{NH}_2$ , which is a substituted ammonia similar to methylamine and ethylamine. As in these the radical is in combination with nitrogen, it is certain that the radical is in combination with nitrogen in the nitro compounds also, as shown in the formula,  $\text{C}_6\text{H}_5\text{NO}_2$ . Everything known about the nitro compounds is in harmony with this view.

In making nitro compounds on the large scale "mixed acid" (a mixture of concentrated nitric and sulphuric acids) is almost invariably used. In the formation of nitro compounds it is highly probable that an addition product is first formed, and that water is eliminated from this by the sulphuric acid reestablishing the double bond (313). In order to form the addition product the un-ionized nitric acid is required, and this is present in the mixed acid. The sulphuric acid combines with the water formed in the reaction, and this prevents the dilution of the nitric acid.

**Mononitrobenzene,  $\text{C}_6\text{H}_5\text{NO}_2$ .**—This substance is made on the large scale by treating benzene with a mixture of ordinary

concentrated nitric and sulphuric acids. Nitrobenzene is a yellow liquid that boils at  $210.9^{\circ}$ , melts at  $5.7^{\circ}$ , and has the specific gravity 1.2193. Its odor is similar to that of the oil of bitter almonds, and it is hence used to some extent instead of the latter. It is known as the *essence of mirbane*. Its vapor is poisonous, when inhaled.

It is slightly soluble in water and the solution has an intensely sweet taste. It mixes in all proportions with alcohol, ether, and benzene. An alcoholic solution gives a red color with a solution of potassium hydroxide, if any *dinitrothiophene* is present. It is used in the preparation of aniline, dinitrobenzene, chloronitrobenzene, benzidine, etc. About  $53\frac{1}{4}$  million pounds were made in the United States in 1920.

**Chloronitrobenzenes,  $C_6H_4(NO_2)Cl$ .** — When monochlorobenzene is nitrated, with mixed acid at ordinary temperatures, about 70 per cent of *p*-chloronitrobenzene and 30 per cent of the ortho product are formed. *m*-Chloronitrobenzene is prepared by chlorinating nitrobenzene in the presence of a carrier. The chlorine in the *o*- and *p*-products can be replaced by hydroxyl, methoxyl, or the amino group by heating them with solutions of the alkalies, with an alcoholic solution of sodium methylete, or with alcoholic ammonia. It is not possible to replace the chlorine in the *m*-product in this way.

**Dinitrobenzene,  $C_6H_4(NO_2)_2$ .** — This is a product of the further action of a mixture of fuming nitric acid and sulphuric acid on benzene, or on nitrobenzene.

*m*-Dinitrobenzene crystallizes in long, yellow needles, or thin, rhombic plates. Melting point,  $89.7^{\circ}$ . About  $2\frac{1}{2}$  million pounds were made in the United States in 1920.

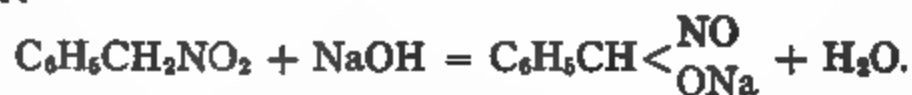
By means of two reactions, which will be described under Diazo Compounds, it is a simple matter to replace the two nitro groups by bromine, thus converting dinitrobenzene into dibromobenzene. When the latter is converted into xylene, the product is metaxylene. Hence, ordinary dinitrobenzene is a meta compound. Small quantities of *o*-dinitrobenzene and traces of *p*-dinitrobenzene are also formed in the nitration of benzene. It is used in the preparation of *m*-phenylene-



diamine, *m*-nitroaniline, and also in the preparation of explosives.

**Chlorodinitrobenzene**,  $C_6H_4Cl(NO_2)_{1,2,4}$ , is made by energetic nitration of chlorobenzene. The chlorine in this compound is extremely easily replaced, *e.g.*, when boiled with a solution of sodium carbonate it gives dinitrophenol,  $C_6H_3(OH)(NO_2)_{1,2,4}$  (377), used in the manufacture of sulphur black. Chlorodinitrobenzene is made on the large scale by nitrating *o*-chloronitrobenzene and is an important dyestuff intermediate. Nearly 6 million pounds were made in the United States in 1920.

**Phenylnitromethane**,  $C_6H_5CH_2NO_2$ , is an example of a nitro compound with the nitro group in the side chain, and is an isomer of the three nitrotoluenes. It is made by the action of benzyl iodide on silver nitrite. It cannot be hydrolyzed, and on reduction gives benzylamine,  $C_6H_5CH_2NH_2$ , and hence is a true nitro compound. When first prepared the substance is a liquid, (b. p.  $225^\circ-227^\circ$ ), somewhat soluble in water, and this solution gives no color with a solution of ferric chloride. When dissolved in a solution of sodium hydroxide it forms a sodium salt,  $C_6H_5CH<\begin{smallmatrix} NO \\ Na \end{smallmatrix}$ , and when this is decomposed in the cold by hydrochloric acid it gives the solid modification (m. p.  $84^\circ$ ), which is unstable and gradually passes over to the liquid form. The solid form (isomeric modification) probably has a formula,  $C_6H_5CH<\begin{smallmatrix} NO \\ OH \end{smallmatrix}$ , similar to that of the sodium salt, since its aqueous solution gives the reddish coloration with ferric chloride solution characteristic of hydroxyl compounds and it reacts very readily with phenyl isocyanate (349). Phenylnitromethane belongs to the class of *pseudo acids*, as it undergoes molecular rearrangement into the true acid before it forms a salt:—



**Nitrotoluenes**,  $C_6H_4(NO_2).CH_3$ . — When toluene is treated with mixed acid, substitution always takes place in the phenyl,

and, on the average, 58.8 per cent of the ortho product is formed, 36.8 per cent of the para, and about 4.4 per cent of the meta by nitration at  $0^{\circ}$ . A higher temperature increases the proportion of the ortho product formed. By treatment with nascent hydrogen, the nitrotoluenes are converted into the corresponding amino compounds, known as *toluidines* (360).

*o*-Nitrotoluene melts at  $-10.5^{\circ}$ , and boils at  $218^{\circ}$ . *p*-Nitrotoluene melts at  $51^{\circ}$ , and boils at  $234^{\circ}$ . They are used in making the toluidines and other dyestuff intermediates. Over 6,000,000 pounds were made in the United States in 1920.

Dinitrotoluene,  $C_6H_5CH_3(NO_2)_2$ , 1,2,4, results from the nitration of *o*- or *p*-nitrotoluene. It melts at  $69.5^{\circ}$ , and on oxidation with nitric acid gives dinitrobenzoic acid. On further nitration it gives symmetrical trinitrotoluene. On reduction it is converted into *m*-toluylenediamine, which is used in the production of azo dyestuffs and sulphur colors.

Symmetrical trinitrotoluene,<sup>1</sup>  $C_6H_2CH_3(NO_2)_3$ , 1,2,4,6, known as T.N.T., is made on the large scale by nitrating toluene in stages with mixed acid. It crystallizes from alcohol in needles, which melt at  $81.5^{\circ}$ . Enormous quantities of this high explosive were used during the World War.

Trinitrotertiarybutyl-*m*-xylene,  $C_6(NO_2)_3<\begin{smallmatrix} (CH_3)_2 \\ C(CH_3)_3 \end{smallmatrix}$ , has an odor similar to that of musk and is known as "artificial musk."

#### AMINO COMPOUNDS OF BENZENE, ETC.

The amino derivatives of the paraffins are made, for the most part, by treating the halogen derivatives with ammonia (100). In treating of these derivatives, however, attention was called to the fact that the primary amines can also be made by treating nitro compounds with nascent hydrogen (104). The latter method is one of great importance in the benzene series. It is used exclusively in the preparation of the amino derivatives of the benzene hydrocarbons. Several of these deriva-

<sup>1</sup> For information concerning explosives the student is referred to the book by Arthur Marshall entitled *Explosives*, 2d edition, 1917.

tives are well known, the simplest and best known being *amino-benzene* or *aniline*.

**Aniline,  $C_6H_7N$  ( $C_6H_5.NH_2$ ).** — Aniline was first obtained from indigo by distillation. *Anil* is the Portuguese and French name of the indigo plant, and it is from this that the name aniline is derived. Aniline is found in coal tar and in bone oil, a product of the distillation of bones. It is prepared by reducing nitrobenzene with nascent hydrogen. On the large scale the hydrogen is obtained from ferrous chloride, iron, and water.

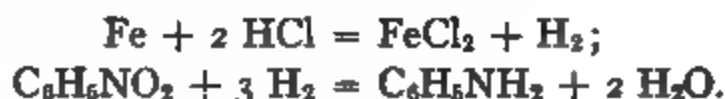
The reactions that take place are as follows: In the presence of iron and water, ferrous chloride is hydrolyzed to ferrous hydroxide and hydrochloric acid: —



The ferrous hydroxide at once reduces some of the nitrobenzene to aniline: —



while the iron reacts with the hydrochloric acid set free to regenerate ferrous chloride and produce nascent hydrogen, which reduces more of the nitrobenzene: —



It will be seen that only a small amount of ferrous chloride is necessary to bring about the reduction of the nitrobenzene to aniline, as the hydrogen comes from the water, and ferrous chloride is constantly regenerated. For laboratory purposes tin and hydrochloric acid are frequently used. Other reducing agents, such as an ammoniacal solution of ammonium sulphide, hydriodic acid, etc., also effect the change.

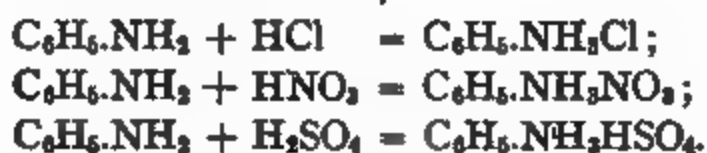
Aniline is a colorless liquid that soon becomes colored brown in the air when not perfectly pure. It boils at  $184.32^\circ$  to  $184.39^\circ$ ; and freezes at  $-6.24^\circ$ . It is somewhat soluble in water (3 parts in 100) and water dissolves in aniline (5 parts in 100). It mixes in every proportion with alcohol, ether, and benzene.

It is very hygroscopic, absorbing water rapidly from the air. The solution in water has a slight alkaline reaction. Aniline is poisonous. Its salts with strong acids have an acid reaction.

A solution of aniline in water gives a violet color with an excess of a solution of chloride of lime, and this reaction is used as a test for aniline.

Aniline is reduced by hydrogen in the presence of colloidal platinum to *cyclohexylamine*,  $C_6H_{11}NH_2$  (b. p.  $135^\circ$ ) which acts like an amine of the paraffin hydrocarbons.

Aniline bears the same relation to benzene that ethylamine or aminoethane bears to ethane. It is a substituted ammonia, and like other amines it unites directly with acids, forming salts. Thus, with hydrochloric, nitric, and sulphuric acids the action takes place as represented below:—



The hydrochloride is known in the trade as *aniline salt*. It is used chiefly in the production of aniline black on the fabric by oxidation.

The decomposition of aniline hydrochloride by means of a caustic alkali takes place as represented in the following equation:—



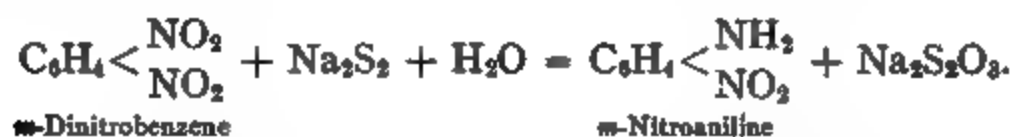
Aniline is used in the preparation of intermediates and dyestuffs. Large quantities are used in the manufacture of synthetic indigo. It is used in the rubber industry, as an accelerator in the vulcanization of rubber. Some idea of its importance in the manufacture of organic chemicals and dyestuffs may be had from the fact that over 39 million pounds were made in the United States in 1920.

**Derivatives of Aniline.** Aniline is much more sensitive to the action of reagents than benzene, chlorobenzene or nitrobenzene. Thus an aqueous solution when treated with chlorine or bromine water precipitates 2,4,6-trichloro- or tribromo-

aniline. The ease with which chlorine and bromine react with aniline is due to the fact that the halogen first substitutes a hydrogen of the amino group, forming phenylbromamide, for example. These halogen amides are exceedingly unstable and immediately undergo molecular rearrangement, the halogen entering the benzene ring in the para and ortho positions:—



As there are two ortho positions and one para in the aniline molecule the reaction stops with the formation of 2,4,6-tribromoaniline. So sensitive is aniline to the action of oxidizing agents that it is frequently necessary to "protect" the amino group. For example, in making the nitroanilines, the nitration is brought about in the presence of large amounts of sulphuric acid, or the aniline is first converted into acetanilide (348). This on nitration gives *p*-nitroacetanilide, as the main product, together with some *o*-nitroacetanilide. On hydrolysis with alkali or acid these yield *p*- and *o*-nitroanilines. *m*-Nitroaniline is made on the large scale by the reduction of one of the nitro groups of *m*-dinitrobenzene (339) with sodium polysulphide:—



The nitroanilines crystallize in yellow needles. The ortho compound melts at 71°, the meta, at 114°, and the para, at 147°. They are not very soluble in water, but dissolve readily in alcohol. The *o*- and *m*-, but not the *p*- product, are volatile with steam, while the *o*- and *p*- compounds, but not the *m*-, undergo hydrolysis when boiled with solutions of the alkalis, giving the nitrophenols:—



*p*-Nitroaniline is made on the large scale and is used principally in the manufacture of the azo dye *p*-nitroaniline red. When

nitrated with mixed acid *m*-nitroaniline gives *tetranitroaniline* (T.N.A.),  $C_6H(NO_2)_4NH_2$ , which is used as an explosive. When reduced the nitroanilines are converted into phenylenediamines,  $C_6H_4(NH_2)_2$ .

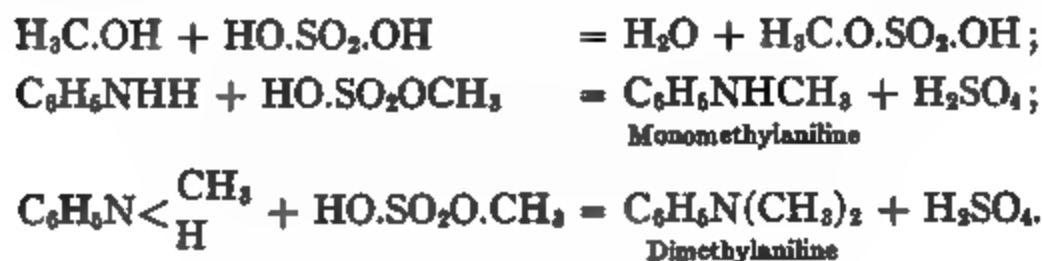
Atoxyl,  $H_2N.C_6H_4.AsO(OH)(ONa)$ , as the formula shows, is a derivative of aminophenylarsinic acid. It is a valuable remedy in sleeping sickness and similar diseases. Its acetyl compound, *arsacetin*, is also used for similar purposes.

*o*-Phenylenediamine,  $C_6H_4(NH_2)_2(o)$ , is best made by reducing *o*-nitroaniline. It crystallizes in colorless leaflets from water, melting at  $102^\circ-103^\circ$ , which rapidly turn brown in the air. Its salts, such as  $C_6H_4(NH_2HCl)_2(o)$ , are more stable. It is much more soluble in water than aniline. It gives a red color with ferric chloride, and is used in the manufacture of sulphur dyes.

*m*-Phenylenediamine is made on the large scale by the reduction of *m*-dinitrobenzene with iron, water, and hydrochloric acid. It forms colorless crystals melting at  $65^\circ$ , which are easily soluble in water, alcohol, and ether. With nitrous acid it is converted into Bismarck brown (364). Even traces ( $\frac{1}{10}$  mg. in a liter) of nitrous acid can be detected by the yellow color it gives with this base. With diazonium salts it gives azo dyes (see Chrysoidine, 364).

*p*-Phenylenediamine, made by reducing *p*-nitroaniline, crystallizes from water and melts at  $147^\circ$ . It gives quinone (431) readily when oxidized with manganese dioxide and sulphuric acid. It is used in the manufacture of dyestuffs and in coloring hair, furs, etc.

Dimethylaniline,  $C_6H_5N(CH_3)_2$ , is made on the large scale by heating aniline, methyl alcohol (which must be free from acetone) and sulphuric acid in an autoclave:—



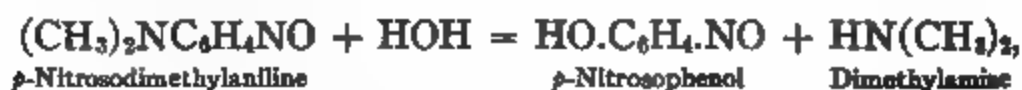
It will be seen from the above reactions that the process resembles the formation of ether from alcohol by the action of sulphuric acid. The sulphuric acid first forms methyl acid sulphate with the methyl alcohol, which reacts with the aniline to give monomethylaniline and regenerates the sulphuric acid. The sulphuric acid set free immediately combines with more alcohol, and the methyl acid sulphate combines with the monomethylaniline to give dimethylaniline and sulphuric acid. The technical dimethylaniline usually contains aniline and some monomethylaniline. A by-product of the manufacture of dimethylaniline is dimethyl ether,  $(\text{CH}_3)_2\text{O}$ , formed by the action of the methyl acid sulphate on the methyl alcohol:—



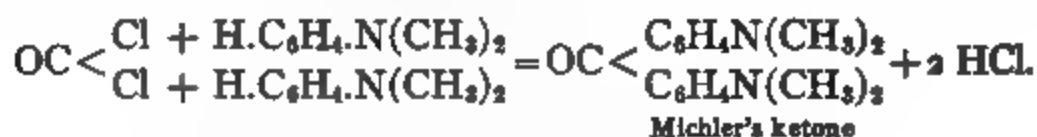
Dimethylaniline is an almost colorless oily fluid, when perfectly pure, which boils at  $193.1^\circ$  and melts at  $2.5^\circ$ . Its specific gravity is 0.955. It is insoluble in water, but soluble in alcohol, ether, and benzene. It is a tertiary amine. The para hydrogen atom is extremely easily replaced. Thus, with nitrous acid it gives *p*-nitrosodimethylaniline:—



which crystallizes in green leaflets melting at  $85^\circ$  and forms a yellow hydrochloride. When warmed with a solution of caustic soda it is hydrolyzed quantitatively into *p*-nitrosophenol and dimethylamine:—



and this is the best method for the preparation of pure dimethylamine. With carbonyl chloride, dimethylaniline gives Michler's ketone (tetramethyldiaminobenzophenone):—

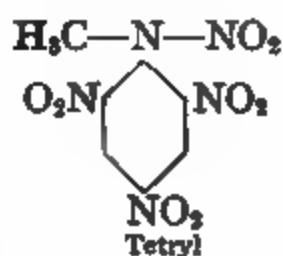


Dimethylaniline combines with formaldehyde (40 per cent solu-

tion) in the presence of hydrochloric acid to give tetramethyldiaminodiphenylmethane:—



When heated with mixed acid dimethylaniline is converted into trinitrophenylmethylnitroamine:



One of the methyl groups is removed by oxidation, its place being taken by a nitro group, while three nitro groups enter the benzene ring. This compound is used as an explosive under the name of *Tetryl*.

Nearly 5½ million pounds of dimethylaniline were produced in the United States in 1920. It is a very important substance, and is largely used in the preparation of intermediates (Michler's ketone and Michler's hydrol, *p*-nitrosodimethylaniline, etc.) and in the manufacture of dyestuffs (Crystal violet, Methyl violet, Malachite green, etc.). It is also used as an accelerator in the vulcanization of rubber.

Diethylaniline,  $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$ , is made on the large scale from aniline and ethyl bromide:—



It is used in the manufacture of rhodamine dyes.

**Diphenylamine**,  $(\text{C}_6\text{H}_5)_2\text{NH}$ .—This is formed from aniline by the introduction of a phenyl group,  $\text{C}_6\text{H}_5$ , for one of the amino hydrogen atoms. It is prepared on the large scale, and finds extensive use in the manufacture of dyes and as an addition to explosives for the purpose of increasing their stability. It is made by heating aniline with aniline hydrochloride at 220°–230° in an autoclave:—





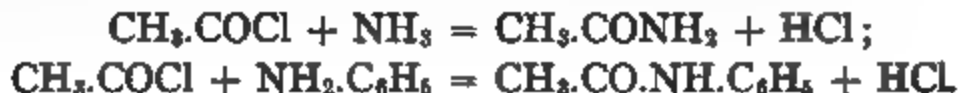
It crystallizes in white laminæ from ligroin (m. p.  $54^{\circ}$ , b. p.  $302^{\circ}$ ). It has a neutral reaction and the odor of flowers. It forms salts with strong acids, but these are decomposed by water. Monomethylaniline and diphenylamine are examples of secondary amines. They both react with nitrous acid, giving nitrosamines:—



Nitrosodiphenylamine, diphenylnitrosamine, crystallizes in yellow plates that melt at  $66.5^{\circ}$ .

The solution of diphenylamine in concentrated sulphuric acid gives an intense blue color with even traces of nitric acid, and this is a very delicate test for nitric acid.

Acetanilide,  $\text{C}_6\text{H}_5.\text{NH}.\text{COCH}_3$ .—Aniline reacts with acid chlorides as ammonia does. While ammonia forms amides, aniline forms *anilides*. Thus, with acetyl chloride, ammonia gives acetamide, and aniline gives acetanilide:—



Acetanilide is made on the large scale by boiling aniline with glacial acetic acid for several days and distilling off the water as fast as it is formed:—



Acetanilide crystallizes from water in large, colorless plates. It melts at  $115^{\circ}$  and boils at  $304^{\circ}$ . It is used in medicine under the name *antifebrine*.

Nearly 3 million pounds were made in the United States in 1920. It is used technically in the preparation of *p*-nitroaniline. Methylacetanilide and ethylacetanilide are used to replace camphor in the celluloid industry.

Phenyglycocoll, phenylglycine,  $\text{C}_6\text{H}_5.\text{NH}.\text{CH}_2\text{COOH}$ , is most readily made by the action of monochloroacetic acid on aniline:—



It is a very important intermediate product in the manufacture of indigo (485).

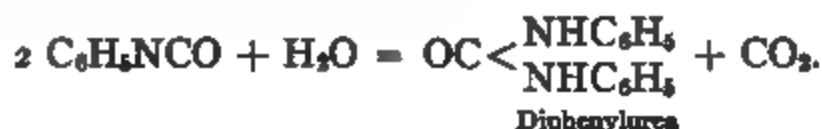
**Hydroxyethylaniline**,  $C_6H_5NHCH_2CH_2OH$ , which is also used in the manufacture of indigo, is made by combining aniline with ethylene chlorhydrin:—



**Phenyl isocyanate**,  $C_6H_5.NCO$ , made from carbonyl chloride and fused aniline hydrochloride:—



is a mobile liquid, boiling at  $163^\circ$  and having a penetrating odor. Its vapor has a marked effect on the mucous membrane of the eyes and nose, producing tears. With water it gives diphenylurea:—

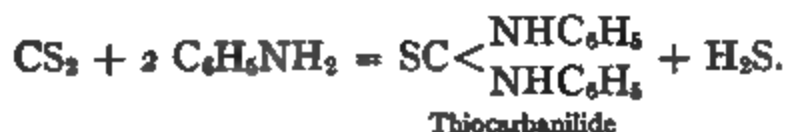


It reacts with alcohols and phenols to form esters of phenylcarbamic acid (phenylurethanes):—



This reaction is characteristic of the alcoholic and phenolic *hydroxyl* group, and is frequently used to determine the presence of this group in organic compounds.

**Thiocarbanilide**, **diphenylthiourea**,  $C_6H_5NHCSNHC_6H_5$ , is made by the action of carbon bisulphide on aniline:—



It crystallizes in leaflets, melting at  $151^\circ$ , which are scarcely soluble in water, but readily in alcohol. It dissolves in alkalis and is precipitated from these solutions by acids, even by carbon dioxide. Large quantities are used as an accelerator in the vulcanization of rubber. Over 2 million pounds were manufactured in the United States in 1920.

**Toluidines, aminotoluenes,  $\text{H}_3\text{CC}_6\text{H}_4\text{NH}_2$ .** — The toluidines, of which there are three corresponding to the three nitrotoluenes, are made from the latter in the same way that aniline is made from nitrobenzene. *Ortho* and *paratoluidine* are used extensively in the manufacture of intermediates and dyes.

The properties of the toluidines are much like those of aniline. *o*-Toluidine is a liquid (b. p.  $199.4^\circ$ ); *p*-toluidine a solid (m. p.  $45^\circ$ ).

The **xylydines** bear to the three xylenes the same relation that aniline bears to benzene. Six isomers are possible and all are known.

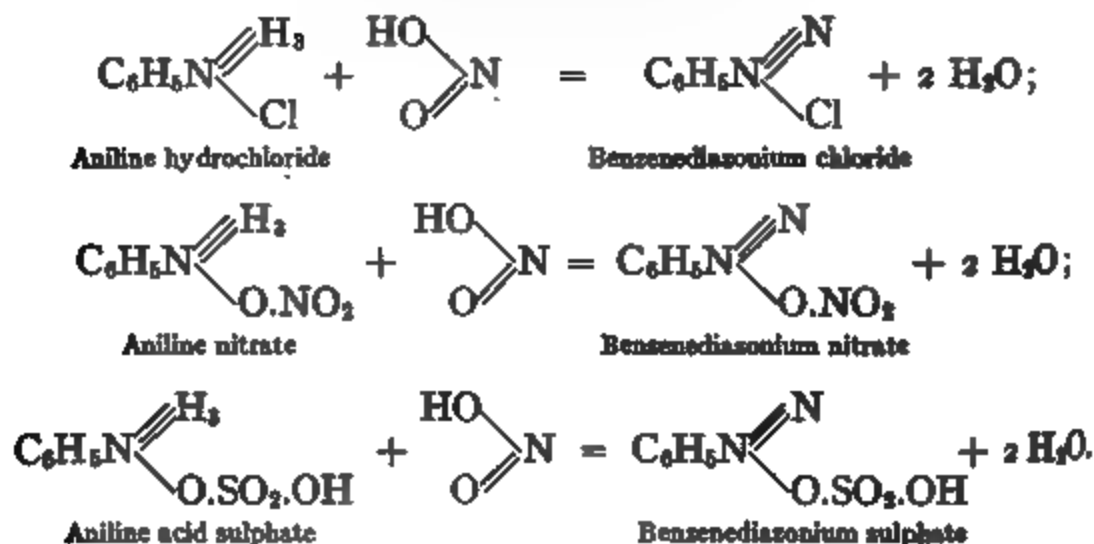
### Diazo Compounds of the Benzene Hydrocarbons

#### DIAZONIUM SALTS

When nitrous acid acts on a *primary* amine of the aliphatic or aromatic series nitrogen is eliminated and hydroxyl takes the place of the amino group: —



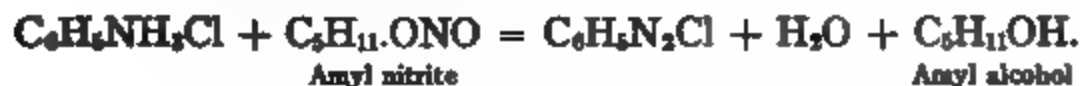
In the case of salts of the aromatic *primary* amines, intermediate products containing two nitrogen atoms and hence first called *diazo* compounds have been obtained. Thus, aniline hydrochloride, nitrate, and acid sulphate react with nitrous acid, provided the temperature of the solution is kept in the neighborhood of  $0^\circ$ , to form *diazonium salts*: —



These salts are called diazonium salts, because they are substituted ammonium salts, as shown in the above formulas, and the process by which they are formed is called *diazotization*. *This property of forming diazonium salts is characteristic of the salts of the aromatic, primary amines.* They are not formed from the aliphatic, primary amine salts, nor are they formed from the secondary or tertiary, aromatic amine salts (see nitrosodiphenylamine (348) and nitrosodimethylaniline (346)). The diazonium salts are characterized by their *instability* (most of them are explosive in the dry state) and the ease with which they react with various substances.

To prepare a solution of benzenediazonium chloride, aniline (one mol.) is dissolved in dilute hydrochloric acid ( $2\frac{1}{2}$  to 3 mols.) and ice is added to bring the temperature in the neighborhood of  $0^{\circ}$ . A solution of the calculated amount of sodium nitrite is then slowly run in from a separatory funnel. The solution must be kept well stirred and the temperature must not be allowed to rise above  $5^{\circ}$ . Owing to the use of diazonium salts in the production of azo dyes (362), this process of diazotization is carried out on the large scale. More than 1000 tons of para-nitroaniline are diazotized annually for the production of the azo dye, paranitroaniline red (357).

To prepare the dry diazonium chloride, aniline hydrochloride is suspended in a mixture of glacial acetic acid and alcohol, and the calculated amount of amyl nitrite is then added to the well stirred, ice-cold solution. The aniline hydrochloride quickly goes into solution as the diazonium chloride. When ether is added to the ice-cold solution the benzene diazonium chloride crystallizes out in colorless needles:—



### REACTIONS OF THE DIAZONIUM SALTS

1. *Replacement of the Diazonium Group by Hydroxyl.*—When the diazonium salts are heated with water, nitrogen is eliminated and hydroxyl derivatives of the aromatic hydrocarbons (phenols) are formed:—



### Phenol

**p. m. p.-Cresol**



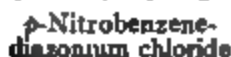
**p. m. p.-Cresol**



### Phenylethylether (Phenetol)



### Aldehyde



### Nitrobenzene

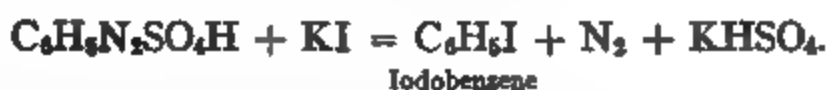
4. *Replacement of the Diazonium Group by Halogens.*—The diazonium group can be replaced by chlorine by treating an aqueous solution of the diazonium salt with a solution of cuprous chloride or with hydrochloric acid in the presence of copper powder:—



Bromobenzene is formed in a similar manner by adding a solution of potassium bromide to a solution of the diazonium salt in the presence of copper powder:—



Iodobenzene is formed when a solution of potassium iodide is added to a solution of the diazonium salt:—



In this case the decomposition of the diazonium iodide first formed takes place spontaneously, no copper powder being necessary. This is the best method of preparing iodobenzene.

5. *Replacement of the Diazonium Group by Cyanogen* takes place when a solution of the diazonium salt is treated with a solution of potassium cuprous cyanide:—



These reactions show the great importance of the diazonium salts in the preparation of numerous derivatives of the benzene hydrocarbons. By their means it is possible to replace the amino group (and hence the nitro group, which is converted into the amino group by reduction) (1) by hydroxyl, (2) by methoxyl or ethoxyl, (3) by hydrogen, (4) by a halogen and (5) by cyanogen. As the cyanides yield acids when hydrolyzed it is thus possible to replace the amino (or nitro) group by carboxyl. The reactions of the diazonium salts have been used very extensively, especially in investigating the position of the groups in the disubstitution products of benzene.

**NOTE FOR STUDENT.** — How can the position of the groups in dinitrobenzene be determined by means of reactions involving the use of the diazonium salts?

*The Constitution of the Diazonium Salts.* — The structure of the diazonium salts is based on the following facts: In all the reactions of the benzene diazonium salts, compounds containing a phenyl group are formed, hence the diazonium group replaces but one hydrogen in benzene. The group  $C_6H_5N_2$  acts like the metals potassium or sodium, or, better still, like a substituted ammonium radical. Thus, with mineral acids it forms colorless salts, having a neutral reaction, similar to potassium or ammonium chloride. Solutions of diazonium carbonates, however, have an alkaline reaction due to partial hydrolysis, just like the carbonates of the alkali metals. Conductivity measurements made with solutions of the diazonium chloride, sulphate, etc., show that these salts are ionized to the same extent as solutions of potassium or ammonium chloride.

Benzenediazonium chloride forms double salts very much like those formed by ammonium chloride. Thus the chloride forms a chloroplatinate,  $(C_6H_5N_2)_2PtCl_6$ , and a chloroaurate,  $(C_6H_5N_2)AuCl_4$ , just as ammonium chloride does. The free base, benzenediazonium hydroxide,  $C_6H_5N_2OH$ , is known only in solution. It is a strong base with an alkaline reaction. It is obtained by treating a solution of the chloride with moist silver oxide and filtering off the silver chloride formed. The solution is colorless and resembles that of caustic potash. It neutralizes the strong acids, forming neutral salts. On standing it gradually undergoes decomposition with the formation of amorphous, resinous substances even at  $0^\circ$ .

#### DIAZO AND ISODIAZO COMPOUNDS OF BENZENE

**Diazobenzene potassium oxide,  $C_6H_5N=N.OK$ .** — When a solution of benzenediazonium chloride, kept cold by means of ice, is treated with an excess of a concentrated solution of caustic potash, diazobenzene potassium oxide is formed: —



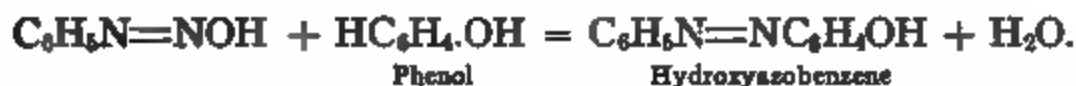
This salt is also formed when nitrosobenzene is treated with hydroxylamine in the presence of caustic potash:—



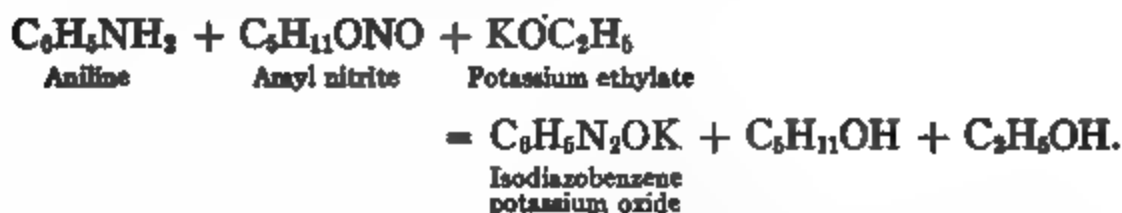
It crystallizes in colorless, hygroscopic needles and is readily soluble in water and alcohol. It is extremely unstable and changes on standing, partly into its isomer, and partly undergoes decomposition. When treated in the cold with a strong mineral acid it is at once reconverted into the diazonium salt:—



With phenols (naphthols) this salt reacts at once to form hydroxyazo compounds (374):—



When the normal diazobenzene potassium oxide is heated rapidly to  $130^\circ$ – $150^\circ$  with a concentrated solution of caustic potash it undergoes molecular rearrangement into its stable isomer, *isodiazobenzene potassium oxide*,  $\text{C}_6\text{H}_5\text{N}_2\text{OK}$ . This salt can also be obtained by diazotizing aniline in alkaline solution:—



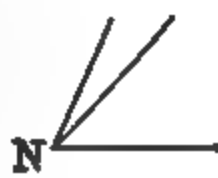
It crystallizes in colorless leaflets, is readily soluble in water and is quite stable. Like its isomer, it is reconverted into the diazonium salts by strong mineral acids and combines in the same way that the normal salts do, *though more slowly*, with phenols (naphthols) to give hydroxyazo compounds. Both salts are reduced quantitatively to phenylhydrazine (360) by nascent hydrogen and both give benzenediazoic acid,  $\text{C}_6\text{H}_5\text{N}=\text{NO.OH}$ , when oxidized with a solution of potassium permanganate.



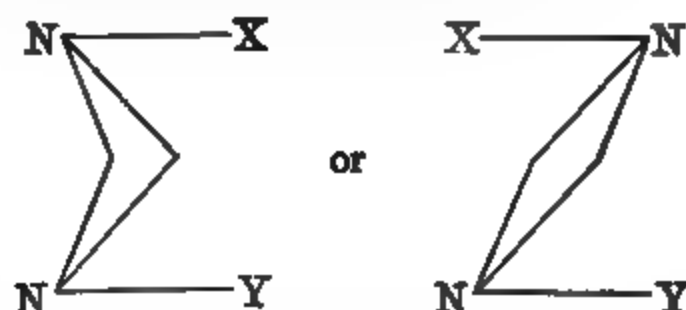
These reactions and others indicate that the two salts are structurally identical and are *stereoisomeric* as represented in the formulas:—



By way of explanation of these formulas, it should be said that they involve the conception that the nitrogen atom exerts its affinities in the direction of three edges of a tetrahedron, thus:—

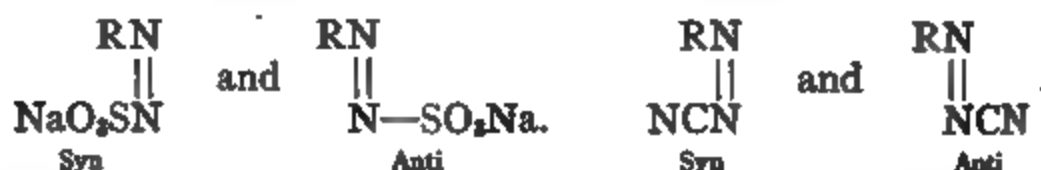


When combined with another nitrogen atom by double union the figures representing this condition would be:—



There are two ways in which the groups or atoms X and Y can be arranged in space, or there should be two stereoisomeric forms of compounds containing a group of two nitrogen atoms of the form  $\text{—N=N—}$  combined with different radicals.<sup>1</sup>

Diazo and isodiazo sulphonates and cyanides, which are regarded as stereoisomeric, are also known, for example:—



*Paranitrobenzene diazonium chloride*,  $\text{O}_2\text{N.C}_6\text{H}_4.\text{N}_2\text{Cl}$ , is made on the large scale from *p*-nitroaniline and converted into the *stable sodium salt* of the *isodiazo* compound,



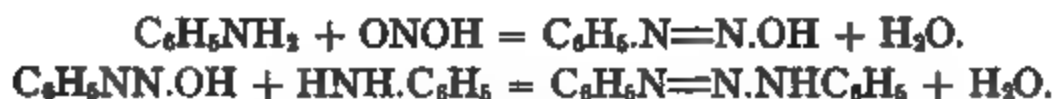
<sup>1</sup> See *Stereochemistry*, by A. W. Stewart, 2d ed., 1919, page 146.

by means of sodium hydroxide, for use of the dyer in dyeing cotton goods with *p*-nitroaniline red. The dyer converts this salt into the diazonium salt by means of hydrochloric acid, using ice to keep the solution cold, and combines this with  $\beta$ -naphthol (500) on the cotton to produce the dyestuff.

**Diazoamino compounds.** — When a diazonium salt is brought in contact with primary or secondary aromatic amines, diazoamino compounds are formed : —



Diazoaminobenzene was first obtained by the action of nitrous acid on aniline. In this case it is probable that diazobenzene hydroxide is first formed and that this then reacts with the aniline, which must be present in excess : —



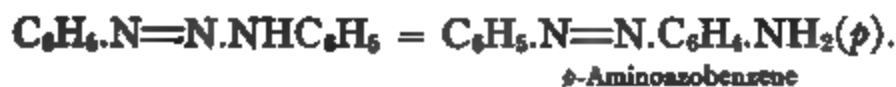
Diazoaminobenzene crystallizes in golden yellow plates that melt at 98°. It is insoluble in water, but is readily soluble in hot alcohol. It is much more stable than the diazonium salts, but undergoes decomposition when boiled with water giving phenol and aniline : —



When treated in the cold with nitrous acid in the presence of hydrochloric acid, diazoaminobenzene is completely converted into benzenediazonium chloride : —



When diazoaminobenzene, dissolved in aniline, is treated with a small quantity of aniline hydrochloride at the temperature of the water bath, it is converted into aminoazobenzene : —



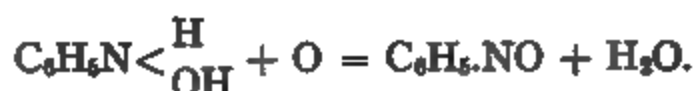
The aniline hydrochloride acts catalytically. This is a very important reaction, and is carried out on the large scale, as aminoazobenzene is an important dyestuff intermediate.

*Other Reduction Products of Nitrobenzene.*—The final reduction product of nitrobenzene is aniline, but intermediate products can be obtained by the use of certain reducing agents.

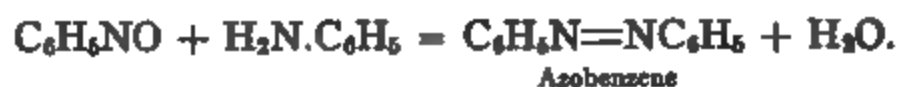
**Nitrosobenzene**,  $C_6H_5NO$ , is the first product of the reduction of nitrobenzene, but it is not possible to isolate it, though its presence can be proved by its reactions, especially that with aniline (see below). It can be made by the action of nitrosyl chloride on mercury diphenyl dissolved in benzene:—



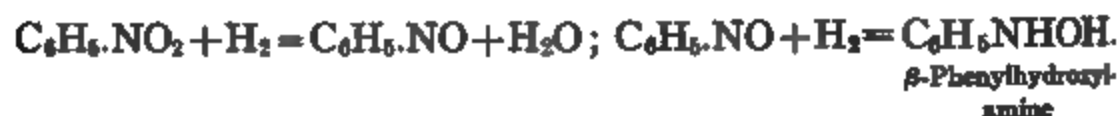
or most readily by the oxidation of  $\beta$ -phenylhydroxylamine (see below) by chromic acid:—



It forms colorless plates, melting at  $68^\circ$ , and when melted is a green liquid. When treated with aniline in acetic acid solution it gives azobenzene (359):—



$\beta$ -Phenylhydroxylamine,  $C_6H_5.N<\begin{smallmatrix} H \\ OH \end{smallmatrix}$ , is formed when nitrobenzene is reduced with zinc dust and water, especially in the presence of ammonium chloride:—



It forms colorless crystals melting at  $81^\circ$ . It undergoes molecular rearrangement in the presence of mineral acids to *p*-aminophenol:—



It reduces Fehling's solution, and this fact is made use of as a test for an aromatic nitro compound. The supposed nitro compound is reduced with water and zinc dust and, if a solution is obtained that reduces Fehling's solution, an aromatic nitro compound is present.

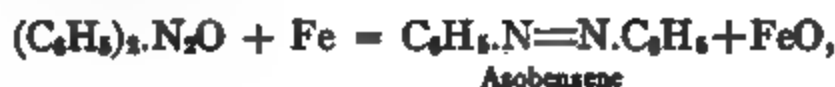
**Azoxybenzene**,  $\text{C}_6\text{H}_5\text{N}(\text{O})\text{N}\cdot\text{C}_6\text{H}_5$ , or  $\text{C}_6\text{H}_5\text{N}(\text{O})=\text{N}\cdot\text{C}_6\text{H}_5$ , is made in the laboratory by reducing nitrobenzene with a methyl alcoholic solution of sodium methylate:—



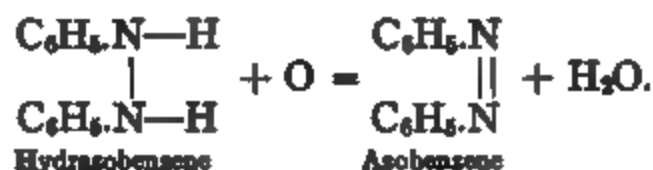
It crystallizes in yellow needles, melting at  $36^\circ$ . It undergoes molecular rearrangement with concentrated sulphuric acid, forming *p*-hydroxyazobenzene:—



**Azobenzene**,  $\text{C}_6\text{H}_5\text{N}=\text{N}\cdot\text{C}_6\text{H}_5$ , is made in the laboratory by heating azoxybenzene with iron filings:—



or better by oxidizing hydrazobenzene (see below) in solution by means of air:—



It has also been made from aniline and nitrosobenzene (358), which shows its structure. It forms orange-red crystals melting at  $68^\circ$ , and boils without decomposition at  $295^\circ$ . It is a very stable substance and can be nitrated and sulphonated in the same way as a hydrocarbon. On reduction with ammonium sulphide it gives hydrazobenzene. Azobenzene can also be very

readily made by the electrolytic reduction of nitrobenzene in the presence of sodium hydroxide. Amino and hydroxy derivatives of azobenzene such as

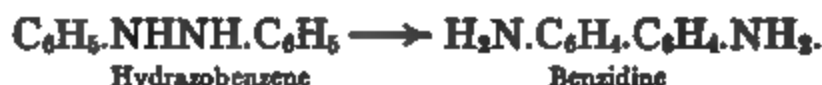


formed by the action of the diazonium salts on aromatic amines and phenols, are also well known. They belong to the important class of azo dyes (382).

Hydrazobenzene,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , is made in the laboratory by the reduction of azobenzene with zinc dust and alkali:—



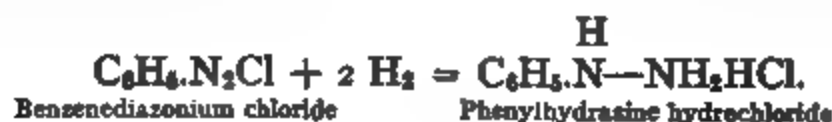
Pure hydrazobenzene crystallizes from alcohol (with the addition of some ammonium sulphide) in colorless leaflets, melting at  $126^\circ$ . Mineral acids convert it quantitatively into benzidine (490):—



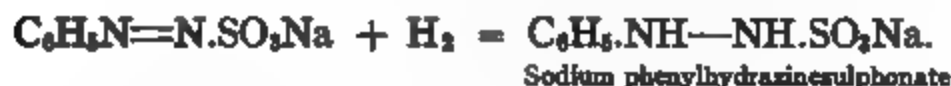
It is made on the large scale by the reduction of nitrobenzene with iron filings and a solution of caustic soda, and converted into benzidine (a very important dyestuff intermediate) by the action of mineral acids.

#### AROMATIC HYDRAZINES

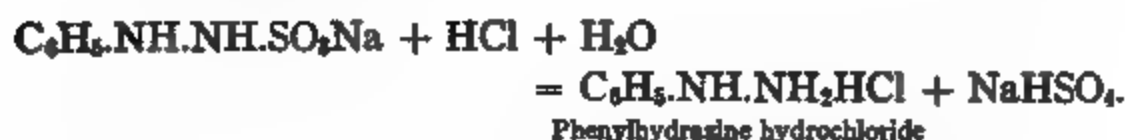
Phenylhydrazine,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2$ , is the simplest aromatic derivative of hydrazine,  $\text{H}_2\text{N}\cdot\text{NH}_2$ . Hydrazobenzene may be regarded as symmetrical *diphenylhydrazine*, though it is never called by this name, as it has no basic properties. Phenylhydrazine is made by the reduction of benzenediazonium chloride, with the calculated amount of stannous chloride, in hydrochloric acid:—



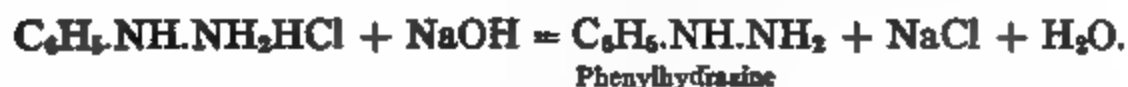
On the large scale it is made by reducing sodium diazobenzenesulphonate with zinc dust and hydrochloric acid:—



The sodium phenylhydrazinesulphonate is then decomposed by fuming hydrochloric acid, in which phenylhydrazine hydrochloride is insoluble:—

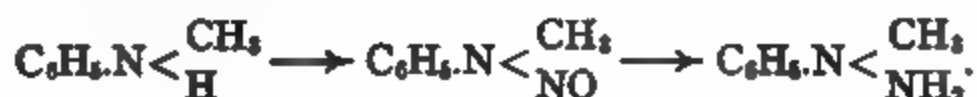


The base is obtained from the hydrochloride by decomposition with caustic soda and is purified by distillation in a vacuum:—



Phenylhydrazine, when perfectly pure, is a colorless oil that quickly turns brown in the air. It solidifies when cooled and the crystals melt at 23°. It boils at 241°–242° with some decomposition. It is volatile with steam, only slightly soluble in water, but miscible with alcohol, ether and benzene. Reducing agents convert it into aniline and ammonia (214). Phenylhydrazine is an exceedingly valuable reagent for aldehydes and ketones, with which it combines to form *phenylhydrazones* (106). It combines with aldoses and ketoses to form phenylhydrazones and osazones (223, 229). Phenylhydrazine is used as a reagent in the laboratory, and in the manufacture of antipyrine and of dyestuffs.

**Methylphenylhydrazine**,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{NH}_2$ , is made from monomethylaniline by treating it with nitrous acid and then reducing the nitrosomethylaniline formed:—



This hydrazine forms osazones with ketoses and also with aldoses, though more slowly.

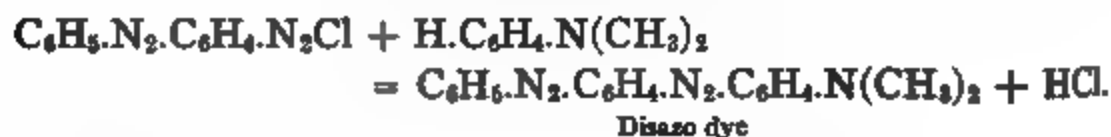
## AZO DYES

The amino and hydroxy derivatives of azobenzene are known as *azo dyes*. They are of great technical importance and are used in large quantities in the dyeing of silk, wool, and cotton.

Azobenzene is a highly colored substance, but it is not a dye. To be a dye a substance must not only be colored, but the color that it imparts to the fabric must be fast to washing and to soap. A group like the azo group,  $\text{—N=N—}$ , which gives color to a compound, is known as a *chromophor*, while the compound containing the chromophor is called a *chromogen*. Thus azobenzene is a chromogen. By introducing a salt-forming group, known as an *auxochrome* group, such as the  $\text{NH}_2$ -group, into a chromogen a *dye* is obtained, *e.g.*, aminoazobenzene is a dye.

Aminoazobenzene,  $\text{C}_6\text{H}_5\text{.N=N.C}_6\text{H}_4\text{NH}_2(p)$ , is the simplest of all the basic azo dyes. It is made on the large scale from diazoaminobenzene by molecular rearrangement (357). It has been made by nitrating azobenzene and reducing the nitroazobenzene formed, which shows its structure.

Its hydrochloride, which crystallizes in steel-blue needles, was used at one time as a dye under the name, *aniline yellow*. Aminoazobenzene crystallizes in orange-yellow needles which melt at  $127.4^\circ$ , and are insoluble in water, but soluble in alcohol. The hydrochloric acid salt can be diazotized and again combined with an amine to give *disazo* dyes, containing *two* azo groups:—



When reduced with nascent hydrogen aminoazobenzene gives aniline and *p*-phenylenediamine:—



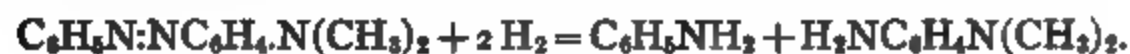
This method of making amino compounds, reduction of the basic azo dyes, is used on the large scale to make *p*-phenylenediamine and other amino compounds. All azo compounds react in a similar manner with nascent hydrogen; the hydrogen always joins the doubly bound nitrogen atoms. From the

amino compounds formed by reduction the structure of the azo dye is determined. Thus, aminoazobenzene gives aniline and *p*-phenylenediamine. It must therefore be an azo compound with the groups in the para position with regard to each other, and it can be made from benzenediazonium salts and aniline. Aminoazobenzene, under the name of *Spirit Yellow*, is used in coloring alcoholic lacquers and also for coloring fats and cheese, as it is not poisonous and is soluble in these substances. It is used chiefly, however, in the manufacture of other dyestuffs (*Acid yellow*, *Cloth red*, *Induline*, etc.).

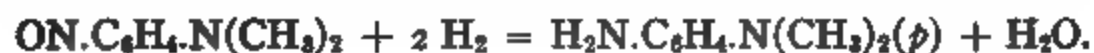
**Dimethylaminoazobenzene**,  $C_6H_5.N=N.C_6H_4.N(CH_3)_2$ . — When a diazonium salt is treated with dimethylaniline, dimethylaminoazobenzene is at once formed, since in this case the formation of a diazoamino compound is not possible: —



As the azo compound here formed is a base, it combines with the acid set free to form a salt. The presence of free mineral acid usually prevents the formation of the azo dyes, so that the "coupling," as it is called, of a diazonium salt with an amine or a phenol is frequently brought about in alkaline solution, or sodium carbonate or acetate is added to get rid of the mineral acid set free in the reaction. When reduced with nascent hydrogen, dimethylaminoazobenzene gives aniline and *p*-amino-dimethylaniline (the dimethyl derivative of *p*-phenylenediamine): —



The main product of the action of a diazonium salt on an amine is always the para product. A small amount of the ortho product is also formed. The reduction of *p*-dimethylaminoazobenzene forms a convenient method of making *p*-amino-dimethylaniline and is used on the large scale, as this base is an important dyestuff intermediate. The same compound is formed by the reduction of *p*-nitrosodimethylaniline (356): —





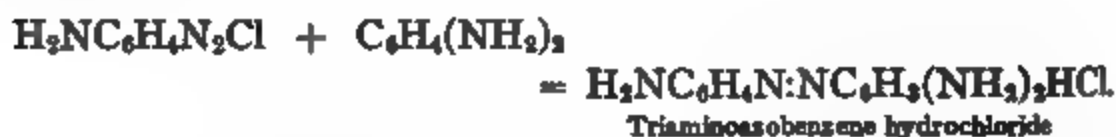
Dimethylaminoazobenzene crystallizes in yellow leaflets, melting at  $117^{\circ}$ . Under the name, *Butter Yellow*, it is used to color butter and oleomargarine, as it is soluble in fats and is not poisonous. It is also used as an indicator.

**Chrysoidine.** — When a benzenediazonium salt is treated with metaphenylenediamine (345), 2,4-diaminoazobenzene is formed: —

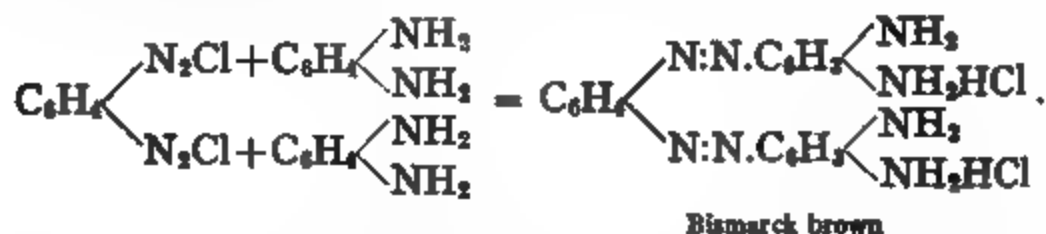


This hydrochloride,  $\text{C}_6\text{H}_5\text{N}:\text{N}:\text{C}_6\text{H}_4(\text{NH}_2)_2\text{HCl}$ , is known as *Chrysoidine*. It dyes wool and silk an orange-red color, and cotton mordanted with tannin an orange color. It is also used to color jute, leather, and fats.

**Bismarck brown** is one of the oldest azo dyes, having been discovered in 1863 and manufactured technically in 1866. It is made by the action of nitrous acid on a salt of *m*-phenylenediamine and is a mixture of at least two substances, the simplest of which is triaminoazobenzene. This is obtained when only one amino group undergoes diazotization, and the diazonium salt thus formed is coupled with a second molecule of the base: —



By far the larger part of Bismarck brown consists of the disazo dye made by diazotizing both amino groups and combining the bi-diazonium salt thus formed with two molecules of *m*-phenylenediamine: —

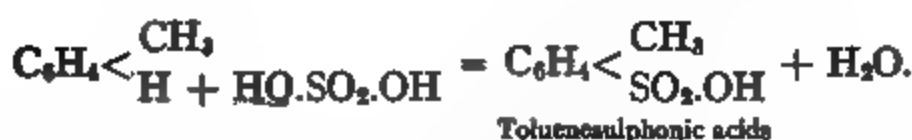
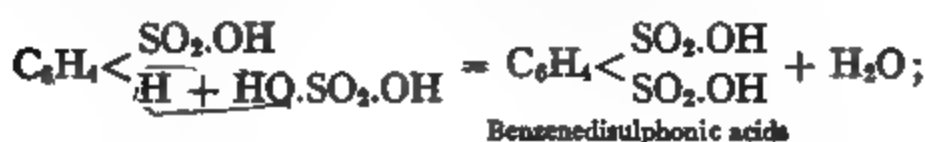


The hydrochloride crystallizes in reddish brown plates and is readily soluble in water. It dyes wool and tanned cotton a red-brown shade.

On reduction with nascent hydrogen Bismarck brown gives *m*-phenylenediamine and 1,2,4-triaminobenzene, and this is the best method of preparing the latter compound.

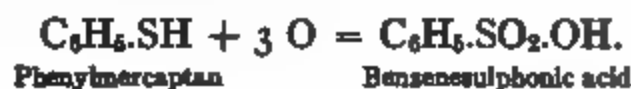
### AROMATIC SULPHONIC ACIDS *Sulphonation*

The aromatic hydrocarbons and their derivatives differ markedly from those of the paraffin series in that they react readily with sulphuric acid to form sulphonic acids:—



This process of forming a sulphonic acid by direct treatment of the hydrocarbon or its derivatives with concentrated or fuming sulphuric acid is called *sulphonation*. The two processes of *sulphonation* and *nitration* are of very great importance in the aromatic series and are more largely made use of than any others in preparing derivatives of these hydrocarbons. A large number of coal tar dyes are sodium salts of aromatic sulphonic acids.

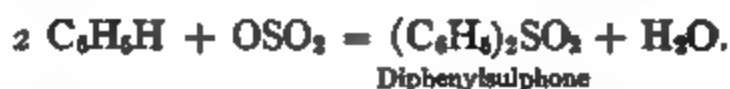
The aromatic sulphonic acids have also been made by the oxidation of the mercaptans:—



The bearing of this method of formation on the question of the constitution of the sulphonic acids has already been discussed (81).

**Benzenesulphonic acid**,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{OH}$ , is made on the large scale by the action of concentrated sulphuric acid (98 per cent) on benzene, and in the laboratory by the action of fuming sulphuric acid on the hydrocarbon. The reaction takes place very readily and without the aid of heat, provided that the benzene and the sulphuric acid are thoroughly mixed.

As in the case of the formation of the aromatic nitro compounds it is probable that an addition product of the hydrocarbon and the acid is first formed and that this then loses water to form the sulphonic acid (313). An excess of sulphuric acid must be used to combine with the water formed in the reaction and thus prevent the dilution of the sulphuric acid. When fuming sulphuric acid is used the *free* sulphur trioxide combines with the water to form sulphuric acid. *Diphenylsulphone* is always formed as a by-product, in the latter case, owing to the action of some of the sulphur trioxide on the benzene:—



The benzenesulphonic acid is separated from the excess of sulphuric acid by diluting the mixture with water and adding lime. The excess of lime and the calcium sulphate are removed by filtration, and the soluble calcium salt is converted into the sodium salt by treatment with a solution of sodium carbonate. A more modern method of separating the two acids makes use of the fact that benzenesulphonic acid is soluble in benzene, while sulphuric acid is not. This process is much more economical than the "limeing out" process, as the excess of sulphuric acid is recovered and may be used over again by adding the right amount of fuming sulphuric acid to bring it up to the proper strength (98 per cent), whereas in the other process the excess of sulphuric acid is converted into the useless calcium sulphate. The benzenesulphonic acid is separated from the benzene by treatment with water, in which it is very soluble, and the benzene, after drying, is used over again. The sulphonic acid is then converted into the sodium salt by the action of sodium carbonate. In the laboratory the sodium benzenesulphonate is "salted out" by adding the mixture of concentrated sulphuric acid and benzenesulphonic acid to a solution of common salt.

Benzenesulphonic acid crystallizes from water in plates containing  $1\frac{1}{2}$  molecules of water of crystallization. It is extremely soluble in water and in alcohol and is a very strong acid. It

forms salts with metals, all of which are soluble in water. It is not hydrolyzed by boiling its solution with strong alkalies or by mineral acids. It is, however, decomposed into benzene and sulphuric acid by distilling in superheated steam in the presence of sulphuric acid:—

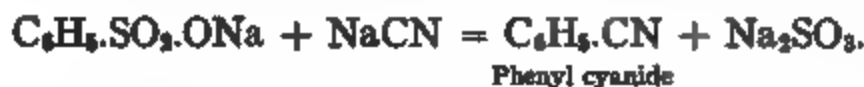


When the sodium salt of benzenesulphonic acid is fused with sodium hydroxide it is converted into the sodium salt of phenol:—



The phenol (372) is set free from its sodium salt by treating the solution with carbon dioxide. This method is used on the large scale in the synthetical production of phenol. It is the most important method of introducing the hydroxyl group into the aromatic hydrocarbons and their derivatives.

When sodium benzenesulphonate is fused with sodium cyanide, phenyl cyanide distils over:—



Like the cyanides of the paraffin series, phenyl cyanide is hydrolyzed by boiling with dilute mineral acids or solutions of the alkalies to the corresponding acid or its salts:—



It is thus possible to convert a sulphonic acid into a carboxylic acid, or to introduce a carboxyl group into an aromatic hydrocarbon or its derivatives. This transformation can sometimes be accomplished directly, *e.g.*, by fusing sodium benzenesulphonate with sodium formate:—



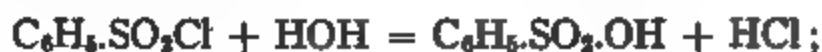
The chloride of benzenesulphonic acid,  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ , is obtained by treating sodium benzenesulphonate with phosphorus pentachloride:—



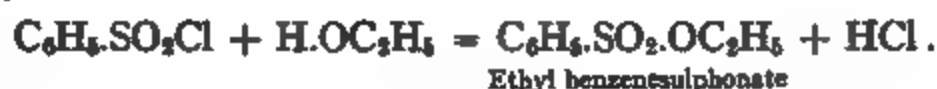
The sulphonyl chlorides can also be obtained by sulphonating the aromatic hydrocarbons with chlorosulphonic acid:—



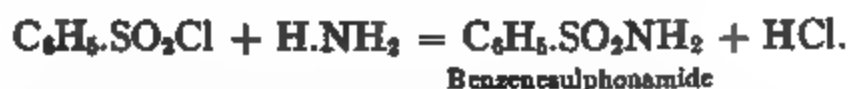
In the case of toluene this method is used on the large scale to make the toluenesulphonyl chlorides (see Saccharin, 412). These chlorides of the sulphonic acids are usually oily liquids or are low melting solids, having a disagreeable odor, and are insoluble in water. When boiled with water, however, they are converted into the acids:—



and when boiled with alcohols into the esters of the sulphonic acids:—



With a strong solution of ammonia they give the sulphonamides:—



Owing to the strong acidifying influence of the sulphon group,  $\text{SO}_2$ , the sulphonamides have acid properties, the hydrogen atoms of the  $\text{NH}_2$  group being replaceable by metals, hence they dissolve in solutions of the alkalis. They are well crystallized solids with sharp melting points, and are frequently used to identify the sulphonic acids.

**Benzenedisulphonic acids**,  $\text{C}_6\text{H}_4(\text{SO}_2\text{OH})_2$ , (*m*) and (*p*), result from the more energetic sulphonation of benzene by heating with fuming sulphuric acid. They undergo the same transformations as the monosulphonic acid.

**NOTE FOR STUDENT.**—By what reactions could the three benzenedisulphonic acids be converted into the three dicarboxylic acids (phthalic acids)? Suppose that the disulphonic acid obtained in larger quantity by sulphonating benzene gave metaphthalic acid; what conclusion could be drawn with reference to the position of the two groups in this disulphonic acid?

Benzenedisulphonic acid is made on the large scale, and converted into resorcinol (385) by fusing its sodium salt with sodium hydroxide.

Toluenesulphonic acids,  $\text{C}_6\text{H}_4\text{CH}_3\text{SO}_2\text{OH}$ , are very readily formed by sulphonating toluene. At  $0^\circ$ , the average yield is 53.5 per cent para, 3.8 per cent meta-, and 42.7 per cent of the ortho acid, while at  $100^\circ$  the percentages are 72.5, 10.1 and 17.4, respectively. When these acids are oxidized they are converted into the corresponding sulphobenzoic acids (411).

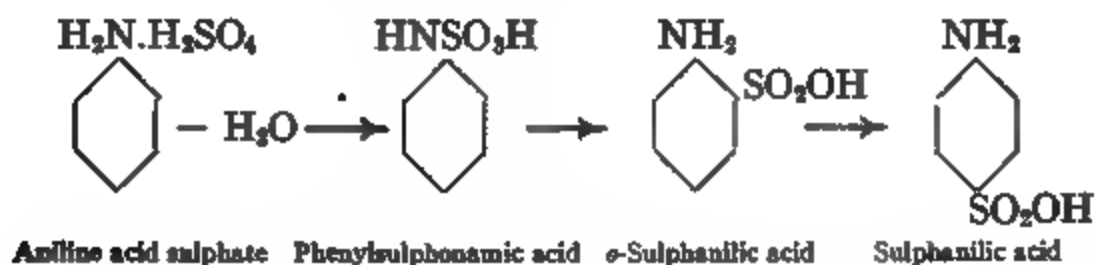
Nitrobenzenesulphonic acids,  $\text{O}_2\text{N.C}_6\text{H}_4\text{SO}_2\text{OH}$ , are obtained by nitrating benzenesulphonic acid or by sulphonating nitrobenzene. In both cases the *meta* acid is the main product. Reduction converts these acids into aminobenzenesulphonic acids,  $\text{H}_2\text{N.C}_6\text{H}_4\text{SO}_2\text{OH}$ .

Metanilic acid,  $\text{H}_2\text{N.C}_6\text{H}_4\text{SO}_2\text{H}(m)$ , obtained in this way, is used in the preparation of azo dyes, *e.g.*, *Metanil yellow* (371).

Sulphanilic acid, *p*-aminobenzenesulphonic acid,

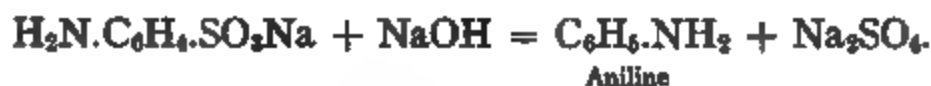


is the most important of the three sulphonic acids derived from aniline. It is always made from aniline acid sulphate by the "baking" process, which consists in baking the acid sulphate in an oven at  $200^\circ\text{--}210^\circ$  from 4 to 6 hours, until a test portion when dissolved in water gives no precipitate (aniline) when made alkaline. The different steps in the process are indicated below:—



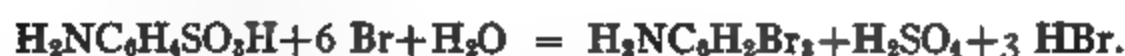
It crystallizes in the monoclinic system with two molecules of water and is difficultly soluble in cold water, more readily in hot. It is a strong acid, decomposing carbonates and forming salts with a neutral reaction, such as sodium sulphanilate,  $\text{H}_2\text{N.C}_6\text{H}_4\text{SO}_2\text{ONa} + 2\text{H}_2\text{O}$ . It does not form salts with acids.

When fused with caustic soda, sulphanilic acid gives *aniline* and not *p*-aminophenol as might have been expected: —



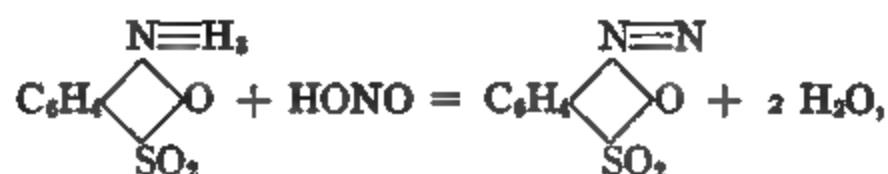
NOTE FOR STUDENT. — Compare this reaction with the one used in making marsh gas from sodium acetate and soda-lime.

Sulphanilic acid also reacts with bromine water in an unusual manner, forming 2,4,6-tribromaniline: —



The sulphonic acid group is replaced by bromine. By determining the amount of sulphuric acid formed in this reaction sulphanilic acid may be estimated quantitatively.

Sulphanilic acid like taurine (254) is an inner ammonium salt. This is shown by the fact that it is diazotized directly by nitrous acid to *benzenediazonium sulphonate*: —

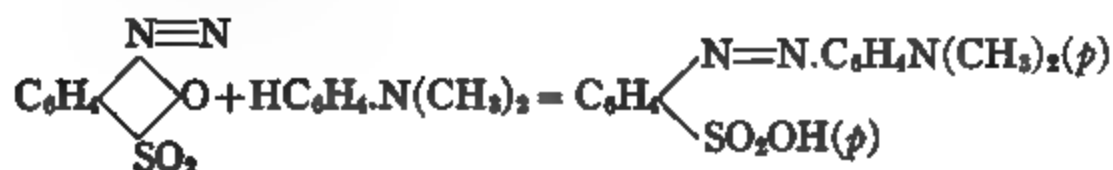


which crystallizes in colorless needles, sparingly soluble in water and shows all the reactions of the diazonium salts. It is used in the manufacture of azo dyes (see below).

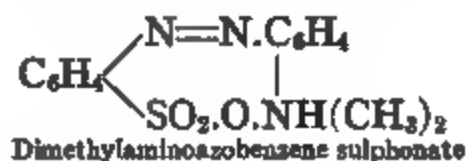
NOTE FOR STUDENT. — What does benzenediazonium sulphonate give when boiled (1) with water, (2) with alcohol, (3) with a solution of potassium iodide and (4) with a solution of potassium cuprous cyanide?

Sulphanilic acid is a very important dyestuff intermediate and is frequently used in synthetical work. Nearly two million pounds were made in the United States in 1920.

**Helianthine**, *p*-dimethylaminoazobenzene-*p*-sulphonic acid, is formed by the action of benzenediazonium sulphonate on dimethylaniline: —

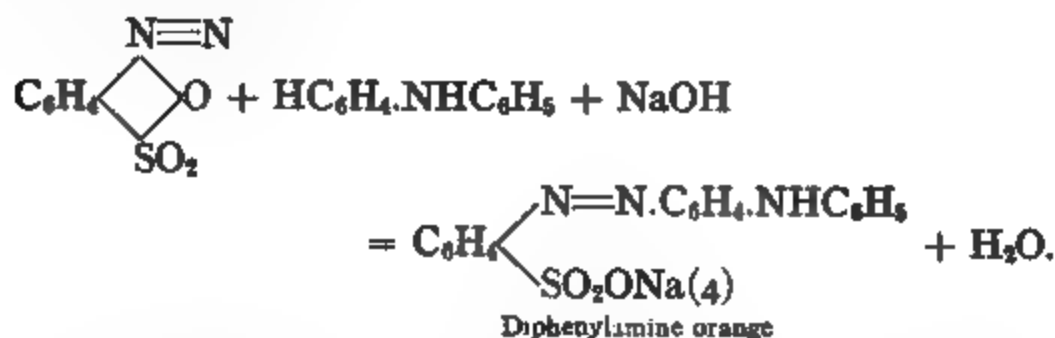


As helianthine contains a basic and an acid group within the same molecule they are probably combined in the form of an inner ammonium salt, as shown in the formula,



The sodium salt of helianthine is known as *methyl orange*. It is not used as a dye, as it is too sensitive to alkalies, but is frequently used as an indicator in acidimetry and alkalimetry. It is not sensitive to carbonic acid, but gives a color with the weakest alkalies, which is turned red by mineral acids.

Diphenylamine orange, orange IV, tropaeolin OO, is another example of a soluble azo dye. It is made by the action of benzenediazonium sulphonate on diphenylamine in the presence of an alkali:—



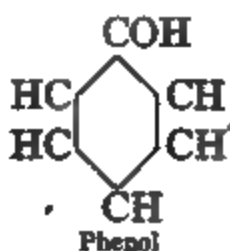
It dyes wool and silk an orange color and is used as an indicator.

**Metanil yellow** is made in the same way from metanilic acid by diazotizing it and combining the diazonium compound with diphenylamine in the presence of an alkali. It has the same formula as diphenylamine orange, only the azo and sulphonic acid groups are in the meta position with reference to each other.

#### PHENOLS OR HYDROXYL DERIVATIVES OF THE AROMATIC HYDROCARBONS

Derivatives of the aromatic hydrocarbons in which the hydrogen of the benzene nucleus is replaced by hydroxyl are called *phenols*, after the first and simplest member of the series, phenol, or hydroxybenzene,



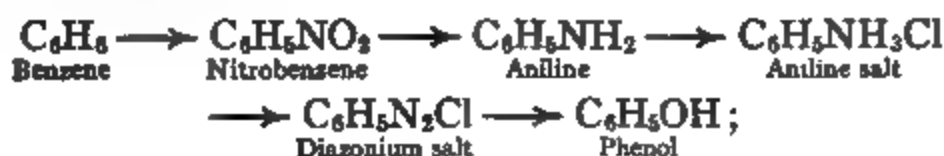


It will be seen from this formula for phenol that it contains the tertiary alcohol group,  $\equiv\text{C}-\text{OH}$ (135), and it acts like an alcohol to some extent. In its conduct towards oxidizing agents phenol acts like the tertiary alcohols, as it gives neither aldehydes nor ketones, but breaks down at once to acids containing a smaller number of carbon atoms. The phenols are, however, more *acid* than the alcohols and dissolve readily in solutions of the caustic alkalies, forming *phenolates*, such as sodium phenolate,  $\text{C}_6\text{H}_5\text{ONa}$ . They are designated as *monacid*, *diacid*, or *triacid* phenols according to the number of hydroxyl groups they contain.

#### MONACID PHENOLS

**Phenol, carbolic acid,  $\text{C}_6\text{H}_5\text{OH}$ ,** occurs normally in small amounts in the urine of men and other animals. It is also found in the distillation products of wood, coal and bones and is obtained from coal tar. Together with the cresols (hydroxytoluenes) and xlenols (hydroxyxylenes) it is isolated from the acid oil (306) by agitation with a 10 per cent solution of caustic soda. The phenols are precipitated from this solution by carbon dioxide, and phenol is separated by fractional distillation from the cresols and xlenols.

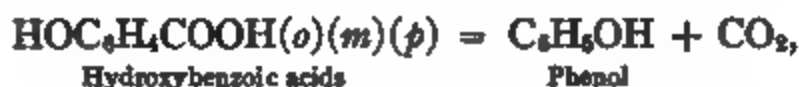
Phenol can also be made synthetically from benzene by the steps indicated below:—



or by fusing sodium benzenesulphonate with caustic soda (367):—



During the World War large quantities of phenol were made by the latter method. Phenol also results from the three hydroxybenzoic acids by distilling them with lime (314):—



and it has been made in small quantity by the direct oxidation of benzene with hydrogen peroxide in the presence of iron salts:—



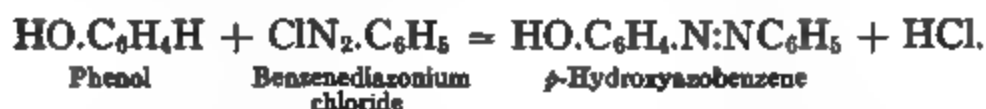
Benzene is oxidized to phenol in the animal organism.

Phenol, when pure, crystallizes in colorless, orthorhombic needles which melt at  $40.8^\circ$  and it boils at  $181.6^\circ$ . In the presence of light and air the crystals soon turn red, due to oxidation. Phenol has a characteristic, penetrating odor and is hygroscopic. A small amount of water lowers the melting point of phenol, so that the mixture is liquid at ordinary temperatures. 8.2 parts of phenol dissolve at  $15^\circ$  in 100 parts of water and 100 parts of phenol at  $15^\circ$  dissolve 37.4 parts of water. At  $84^\circ$  phenol is miscible with water in all proportions. It mixes in all proportions with alcohol, ether, and benzene and is poisonous. Saccharate of lime or sodium sulphite is used as an antidote in cases of poisoning with phenol. Phenol is a valuable disinfectant and antiseptic, though its use for this purpose is diminishing, as *m*-cresol has been found to have greater disinfecting power and to be less poisonous. Phenol is a weak acid having about the same strength as hydrocyanic acid. It is set free from its solution in ammonia or the alkalies by carbon dioxide and hence is not soluble in solutions of the alkaline carbonates. Towards methyl orange and phenolphthalein phenol acts like a neutral substance, but it acts as a monobasic acid towards Poirrier's blue. When reduced with hydrogen at  $160^\circ$  in the presence of nickel as a catalyst, phenol is quantitatively reduced to *cyclohexanol*,  $\text{C}_6\text{H}_{11}\text{OH}$ , a secondary alcohol, boiling at  $161^\circ$ , and melting at  $16^\circ$ – $17^\circ$ . When platinum black is used as a catalyst cyclohexane is formed. When cyclohexanol

is oxidized it gives *cyclohexanone*,  $C_6H_{10}O$ , a ketone, thus showing that it is a secondary alcohol. (Write the equations involved in all these transformations.)

Most of the phenol is used in the manufacture of picric acid (378), salicylic acid (420), dyes and synthetic remedies. Large quantities are now used in making synthetic resins (for phonograph records, bakelite, etc.) by combining phenol with formaldehyde. Synthetic tanning materials are also now made from phenol, formaldehyde, and sulphuric acid or sulphites. Triphenyl phosphate is now made on the large scale from phenol and used as a substitute for camphor in the manufacture of pyroxyline plastics (376).

Like aniline phenol is extremely susceptible to the action of reagents. The hydrogen of the hydroxyl group is first replaced by the substituting group or element, which then enters the benzene ring, hydrogen taking its place. Thus, a solution of phenol in water gives a precipitate of tribromophenol bromide,  $C_6H_3Br_3.OBr_{2,4,6}$ , when treated with bromine water, and *dilute nitric acid* converts it into ortho- and paranitrophenol. The best test for phenol (in the absence of cresols) is the precipitate it gives with bromine water. One part of phenol in 44,000 parts of water gives a perceptible precipitate at once with this reagent. Millon's reagent gives a yellow precipitate with phenol solutions, and this test is said to be more delicate than the reaction with bromine water. A solution of ferric chloride gives a blue-violet color with neutral solutions of phenol. Like aniline and its derivatives phenol and its derivatives react readily with benzenediazonium salts to form azo dyes. In alkaline solution it gives *p*-hydroxyazobenzene and a small amount of the *o*-compound: —



**p-Hydroxyazobenzene** crystallizes in orange colored, rhombic prisms melting at  $152^\circ$ , and is a yellowish red dyestuff. It is also formed by the molecular rearrangement of azoxybenzene

(359) with sulphuric acid and by heating *p*-nitrosophenol with aniline acetate at 100°:—

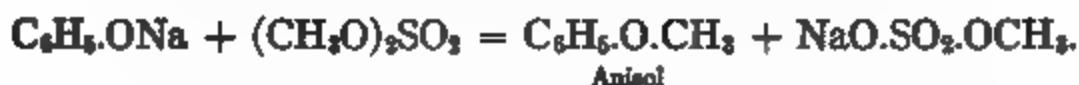


This last reaction shows the structure of the compound.

*p*-Hydroxyazobenzene is no longer used as a dye. Large quantities of it are made, however, from phenol and diazotized aniline for the manufacture of *p*-aminophenol. For this purpose the *p*-hydroxyazobenzene is reduced with iron and hydrochloric acid (write the equation), and the aniline formed is separated from the *p*-aminophenol by distillation in steam and is used over again.

Like the alcohols phenol forms ethers and esters.

**Methylphenyl ether, anisol**,  $\text{C}_6\text{H}_5.\text{O}.\text{CH}_3$ , was first obtained from anisic acid (methoxybenzoic acid) by distilling it with barium oxide, and hence the name. It is best made by treating a solution of sodium phenolate with dimethyl sulphate:—



It is a pleasant smelling liquid melting at  $-37.8^\circ$  and boiling at  $153.9^\circ$ . It was used during the World War as a delousing agent. It is used as a solvent, in the preparation of trinitro-anisol and of methoxyacetophenone (formed by the action of acetyl chloride on anisol and used in the manufacture of perfumes).

**Ethylphenyl ether, phenetol**,  $\text{C}_6\text{H}_5.\text{O}.\text{C}_2\text{H}_5$ , is made from sodium phenolate and ethyl bromide:—

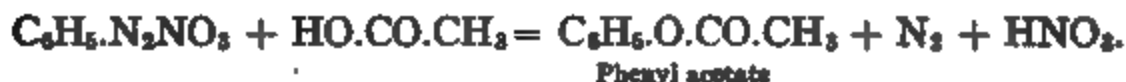


It is a liquid with a pleasant odor, melting at  $-33.5^\circ$  and boiling at  $171.5^\circ$ – $172.5^\circ$ .

**NOTE FOR STUDENT.**—Compare these two substances with the *mixed ethers* (46). What method analogous to the one used in the preparation of phenetol is used in the preparation of mixed ethers? Does phenol act like an alcohol? How are these phenol ethers made from aniline?

**Diphenyl ether,  $C_6H_5.O.C_6H_5$** , is made on the large scale by the action of bromobenzene on potassium phenolate in the presence of finely divided copper at  $210^\circ$ . (Write the equation.) It melts at  $28^\circ$  and boils at  $252^\circ$ – $255^\circ$  and has an odor similar to that of the geranium. It is used in the manufacture of perfumes.

Phenyl acetate,  $C_6H_5.O.CO.CH_3$ , is formed when phenol is treated with acetyl chloride or when a benzenediazonium salt is boiled with glacial acetic acid : —



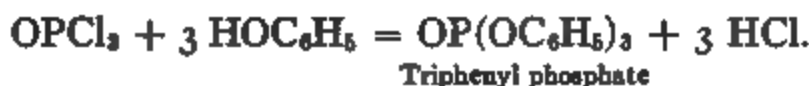
**It is a liquid boiling at 195°.**

**NOTE FOR STUDENT.** — Write the equation of the reaction that takes place when acetyl chloride acts on phenol.

**Phenol also forms esters of the inorganic acids, e.g.:—**

**Phenylsulphuric acid,  $C_6H_5.HSO_4$ .**— This is present in human urine in the form of the potassium salt.

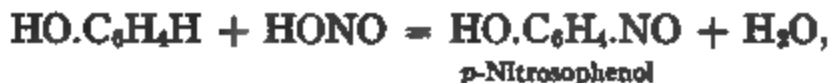
**Triphenyl phosphate**,  $\text{OP}(\text{OC}_6\text{H}_5)_3$ , is made by the action of phosphorus oxychloride on phenol:—



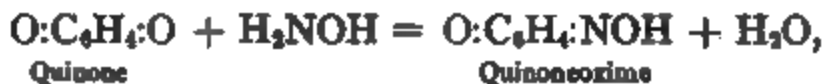
**Triphenyl phosphate** melts at 45°. It is used as a substitute for camphor in the manufacture of pyroxyline plastics.

## SUBSTITUTION PRODUCTS OF PHENOL

***p*-Nitrosophenol**,  $\text{HO.C}_6\text{H}_4.\text{NO}$  (*p*), or **quinone oxime**,  $\text{O:C}_6\text{H}_4.\text{NOH}$ , is made by the action of nitrous acid on phenol:—



or by the action of solutions of the alkalis on *p*-nitrosodimethylaniline (346). Since it is also formed by the action of hydroxylamine hydrochloride on quinone (433):—



it is highly probable that it is an oxime of quinone as shown above. It crystallizes in yellowish needles, is fairly soluble in water, readily in alcohol, ether, and acetone, and the solutions have a bright green color. Like the oximes it has acid properties, the hydrogen of the  $=\text{NOH}$  group being replaceable by metals and radicals. When reduced with sodium sulphide it gives *p*-aminophenol and, when oxidized, *p*-nitrophenol. (Write the equations.) It is made on the large scale from phenol and is used in the manufacture of the hydron dyes (especially hydron blue), the sulphur dyes, and of *p*-aminophenol.

**Nitrophenols,  $\text{HO.C}_6\text{H}_4.\text{NO}_2$ .**—Nitration of phenol with dilute nitric acid produces about equal quantities of ortho- and paranitrophenol, which are separated by distillation in steam, the ortho product being volatile. *o*-Nitrophenol crystallizes in yellow, orthorhombic needles, having a characteristic penetrating odor and a sweet taste. It is slightly soluble in cold water, readily in alcohol and ether, melts at  $44.5^\circ$  and boils at  $214^\circ$ . On reduction it gives *o*-aminophenol. Its salts with the metals have a red color. Together with *p*-nitrophenol it is made on the large scale by nitrating phenol, and is used in making *o*-nitroanisole, *o*-aminophenol, dianisidine, etc., and in the manufacture of azo and sulphur dyes. *p*-Nitrophenol crystallizes in colorless needles, melting at  $114^\circ$ . It is fairly soluble in hot water, readily in alcohol, and its salts with the metals have a yellow color. On reduction it gives *p*-aminophenol. It is used in the manufacture of *p*-aminophenol, *p*-nitrophenetol, sulphur dyes (Vidal black), and also in the laboratory as an indicator.

*m*-Nitrophenol is made from *m*-nitroaniline (344) by diazotizing its hydrochloride and decomposing the diazonium salt with water. The nitrophenols are stronger acids than phenol, e.g., they decompose carbonates, forming salts and setting carbon dioxide free. <sup>1</sup>

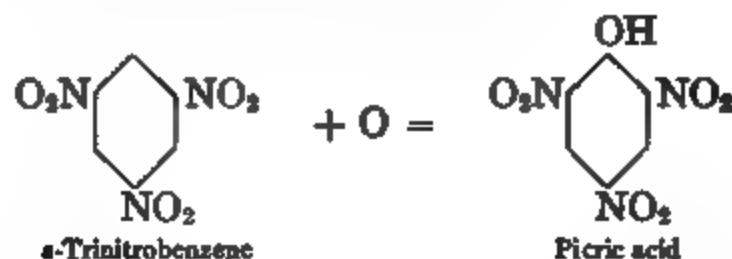
**Dinitrophenol,  $\text{C}_6\text{H}_3(\text{OH})(\text{NO}_2)_{2,1,2,4}$ ,** is made by boiling 1-chloro-2,4-dinitrobenzene (340) with sodium carbonate, and is used in making sulphur dyes. When nitrated it gives picric acid (378). On reduction it gives 2,4-diaminophenol, used as a photographic developer under the name of *amidol*.

*s*-Trinitrophenol, picric acid,  $\text{HO.C}_6\text{H}_2(\text{NO}_2)_3$ , 1,2,4,6, is made on the large scale, for use as an explosive, by dissolving phenol in concentrated sulphuric acid and treating the phenolsulphonic acids formed (381) with nitric acid (sp. gr. 1.4) : —



NOTE FOR STUDENT. — Compare this reaction with that of bromine on sulphanilic acid (370). What does sulphanilic acid give when fused with caustic soda?

During the World War large quantities of picric acid were made from chlorobenzene. This when nitrated gives 1-chloro-2,4-dinitrobenzene, which is converted into 2,4-dinitrophenol by boiling with soda solution. This gives picric acid when nitrated. Picric acid also results from the oxidation of *s*-trinitrobenzene with potassium ferricyanide : —



This reaction and the fact that picric acid is obtained by the nitration of *o*- and *p*-nitrophenol, but cannot be made by the nitration of *m*-nitrophenol, determines its structural formula. Picric acid is also formed by the action of nitric acid on silk, leather, various resins, indigo, and aniline. Picric acid crystallizes from water in yellow leaflets which melt at  $122.5^\circ$ . There are two modifications of picric acid, one yellow, the other colorless. The solution in water has a deep yellow color and contains the yellow form, while the solution in ligroin is colorless. When the sodium salt of picric acid is reduced with sodium hydrosulphide, *picramic acid*,  $\text{C}_6\text{H}_2(\text{NO}_2)_2.\text{NH}_2(\text{OH})$  (4,6-dinitro-2-aminophenol), is formed. This crystallizes in red needles, melting at  $168^\circ$ – $169^\circ$ . It is used in the manufacture of azo dyes. Picric acid is a strong acid, comparable with the mineral acids, and like the strong acids undergoes considerable ionization in

aqueous solution. The presence of the three nitro groups has a remarkable influence on the phenol hydroxyl group, so that in its reactions picric acid resembles the carboxylic acids, *e.g.*, it gives *picryl chloride*,  $C_6H_2(NO_2)_3Cl$  (trinitrochlorobenzene) with phosphorus pentachloride, which can also be made by the nitration of chlorobenzene. This reacts like the chloride of an acid, giving picric acid when boiled with water; *picramide*,  $C_6H_2(NO_2)_3NH_2$  (trinitroaniline), with ammonia; and esters with alcohols, such as trinitroanisole,  $C_6H_2(NO_2)_3OCH_3$ , which can also be obtained by nitrating anisole. (Write all the equations.) Picric acid forms well crystallized salts. The ammonium salt, which is used as an explosive, exists in a yellow and a red modification. Picric acid is one of the oldest dyes, having been first used in dyeing silk in 1849. It dyes wool, silk and the human skin an intense yellow. It is no longer used as a dye. Picric acid has an extremely bitter taste and hence the name (Gr. *pikros*, bitter). With bleaching powder picric acid gives *chloropicrin*,  $CCl_3NO_2$ , one of the "poison gases" used during the World War. Under the name of *lyddite*, picric acid is used as a high explosive.<sup>1</sup>

**Aminophenols,  $HO.C_6H_4.NH_2$ .**—The aminophenols are formed by the reduction of the nitrophenols.

*o*-Aminophenol crystallizes in colorless scales which melt at  $174^\circ$  and quickly turn brown in the air due to oxidation. It is soluble in water, alcohol, and ether and has basic properties forming a hydrochloride,  $HO.C_6H_4.NH_2.HCl$ , crystallizing in colorless needles. The methyl ether,  $H_3CO.C_6H_4.NH_2$ , known as *o*-anisidine, is made by the reduction of *o*-nitroanisole and is used in the preparation of azo dyes and in the manufacture of guaiacol (384).

*Salvarsan*, a valuable remedy in sleeping sickness, syphilis, and similar diseases, is the hydrochloride of diaminodihydroxy-arsenobenzene,

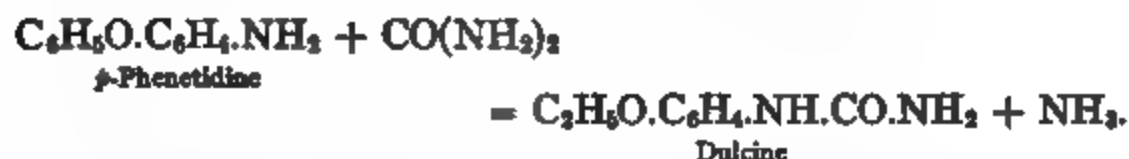


<sup>1</sup> See *Explosives*, by Arthur Marshall, 2d edition, 1917.





**Dulcine** or **Sucrol**,  $C_2H_5O.C_6H_4.NH.CO.NH_2$ , is made by heating *p*-phenetidine with urea:—



It is 200 times as sweet as cane sugar and was used during the World War as a sweetening agent in place of sugar.

**Phenacetine**,  $C_2H_5O.C_6H_4.NH.COCH_3$ , made from *p*-phenetidine by heating with glacial acetic acid (see Acetanilide, 348), is used in medicine as an antipyretic and antineuralgic. It is said to be less poisonous than acetanilide.

**Phenolsulphonic acids**,  $HO.C_6H_4.SO_2OH$ .—Phenol is sulphonated much more readily than benzene. It forms *o*- and *p*-phenolsulphonic acids when treated with sulphuric acid at ordinary temperatures. *o*-Phenolsulphonic acid is unstable and goes over into the para acid when heated. Even heating its aqueous solution transforms it into a solution of the para acid. When phenol is sulphonated at 100° the para acid is therefore the main product. These acids are the intermediate products in the manufacture of picric acid (378). *Aseptol* is a 33½ per cent aqueous solution of *o*- and *p*-phenolsulphonic acids and is used as an antiseptic.

*m*-Phenolsulphonic acid is obtained by fusing benzenedisulphonic acid (368) with caustic soda:—



It is an intermediate product in the manufacture of resorcinol (385).

**Cresols, hydroxytoluenes, cresylic acids**,  $HO.C_6H_4.CH_3$ .—The three cresols are present in the acid oil and naphthalene fraction (306) obtained in distilling coal tar, and are separated from phenol (372) and the xylenols by fractional distillation. The cresols are also present in pine wood and beech wood tars. The coal tar cresol is a mixture of 35 to 40 per cent ortho-, 35 to 40 per cent meta-, and 25 per cent para-cresol. Nearly pure *o*-cresol can be obtained from this mixture by careful

fractional distillation. The remaining mixture, containing 60 per cent meta- and 40 per cent para-cresol, is separated by treating it with three times the quantity of fuming sulphuric acid (20 per cent  $\text{SO}_3$ ). Sulphonation takes place in the cold. Water is then added so that the boiling point of the solution is  $125^\circ\text{--}130^\circ$ . When superheated steam is run in, the *m*-cresol-sulphonic acid is hydrolyzed and *m*-cresol distils over with the steam. After all the *m*-cresol has distilled over, the *p*-cresol-sulphonic acid is hydrolyzed at a higher temperature with superheated steam and the *p*-cresol distils with the steam. The pure cresols can also be obtained from the corresponding toluidines (350, 353) or from the toluenesulphonic acids by fusing the latter with caustic soda.

NOTE FOR STUDENT — Write the equations representing the reactions involved in these transformations.

The cresols resemble the phenols closely in their properties. They are weaker acids, but are stronger antiseptics than phenol. *m*-Cresol is the most efficient bactericide and the least poisonous. *o*-Cresol melts at  $31^\circ$  and boils at  $188^\circ$ . *m*-Cresol melts at  $4^\circ$  and boils at  $203^\circ$ , while *p*-cresol melts at  $36.5^\circ$  and boils at  $202^\circ$ . Both the *m*- and the *p*-cresol, but not the ortho, give a blue color with a solution of ferric chloride. Artificial resins are made from the cresols by condensing them with formaldehyde. The resin made from *o*-cresol is without odor and is used as a substitute for shellac. Synthetic tanning materials are also made from the cresolsulphonic acids by combining them with formaldehyde.

Thymol, *p*-isopropyl-*m*-cresol,  $\text{H}_3\text{CC}_6\text{H}_3(\text{OH})\text{CH}(\text{CH}_3)_2$ , occurs in various essential oils, especially in the oil of thyme, whence the name. On the large scale it is obtained from Ajowan oil by shaking it with a 10 per cent solution of caustic soda. The aqueous alkaline solution of the thymol is separated from the *p*-cymene and terpenes present in the oil, and the thymol is precipitated by acid and purified by recrystallization. It forms large transparent, hexagonal crystals melting at  $51.5^\circ$ , and it boils at  $232^\circ$ . It is used in medicine and as an antiseptic. When

heated with phosphorus pentoxide, it yields *m*-cresol and propylene, while, when distilled with phosphorus pentasulphide, it gives cymene. These two reactions show that thymol is *p*-isopropyl-*m*-cresol. (Write the equations.)

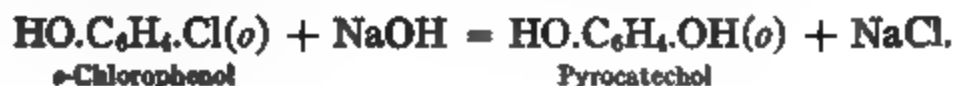
When treated with iodine and a solution of caustic soda, thymol gives a diiododithymol, a derivative of diphenyl. Under the name *aristol* this substance is used as a substitute for iodoform.

Carvacrol, *p*-isopropyl-*o*-cresol,  $\text{H}_3\text{CC}_6\text{H}_3(\text{OH})\text{CH}(\text{CH}_3)_2$ , occurs in the oil of thyme and in camphor oil. It constitutes about 80 per cent of the oil of *Origanum hirtum*. It is obtained from its isomer, carvone, which is the chief constituent of the oil of caraway, by heating this ketone with glacial phosphoric acid. It is closely connected with camphor and can be obtained by heating camphor with iodine. It has also been made from cymenesulphonic acid by fusing it with caustic soda. When pure it is a colorless liquid melting at about  $1^\circ$ , and boiling at  $236^\circ$ – $237^\circ$ . It is distinguished from its isomer, thymol, by the fact that it gives a green color with a solution of ferric chloride. With phosphorus pentoxide it gives *o*-cresol and propylene, while with the pentasulphide it gives *p*-cymene. These two reactions show its structure.

### DIACID PHENOLS

The three dihydroxybenzenes,  $\text{C}_6\text{H}_4(\text{OH})_2$ , are well known and all are important substances. *m*-Dihydroxybenzene, resorcinol, is the most important.

Pyrocatechol, *o*-dihydroxybenzene,  $\text{C}_6\text{H}_4(\text{OH})_2$ , occurs in raw beet sugar and was first made by the distillation of catechin (*Mimosa catechin*), whence the name pyrocatechin formerly used. Many other resins give pyrocatechol when distilled or when fused with caustic alkalies. It is made on the large scale from phenol. When chlorine is passed into phenol the main product is *o*-chlorophenol. This is converted into pyrocatechol by heating with a solution of caustic alkali:—



**NOTE FOR STUDENT.** — Can chlorine be removed from chlorobenzene by boiling it with a solution of an alkali? What is the effect of heating the three chloronitrobenzenes with aqueous alkali? What does picryl chloride give when boiled with water?

Pyrocatechol crystallizes in monoclinic prisms. It melts at  $104^{\circ}$  and boils at  $245^{\circ}$  and is soluble in water, alcohol and ether. Like phenol it combines with sulphuric acid to form an acid sulphate and in this form it is a constant constituent of the urine of horses. It is more susceptible to the action of reagents than phenol, e.g., it reduces a solution of silver nitrate in the cold and Fehling's solution on warming. Its aqueous solution becomes green on the addition of a solution of ferric chloride, and this color changes to a violet when a solution of soda or sodium acetate is added. Lead acetate gives a precipitate of the lead salt, and calcium chloride, in the presence of ammonia, crystals of the calcium salt. These reactions distinguish pyrocatechol from its isomers, resorcinol and hydroquinol. The alkaline solution turns brown in the air due to oxidation.

Pyrocatechol is used as a photographic developer and in the manufacture of guaiacol and adrenalin.

Guaiacol,  $\text{HO.C}_6\text{H}_4.\text{OCH}_3(o)$ , occurs in guaiac resin and in beech wood tar and was formerly obtained from this source. It was then made on the large scale from an alkaline solution of pyrocatechol and sodium methyl sulphate. (Write the equation.) At present it is made by diazotizing a salt of *o*-anisidine and boiling the product with water: —



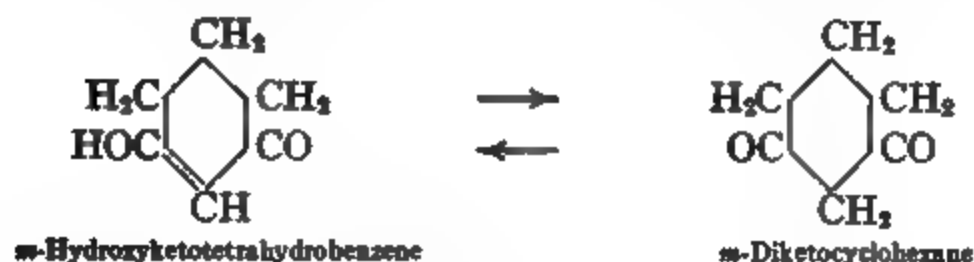
It forms colorless crystals that melt at  $28.5^{\circ}$ , and it boils at  $205^{\circ}$ . It has a characteristic odor and a sweet taste. It is somewhat soluble in water and readily in alcohol and ether. The alcoholic solution gives a blue color with a solution of ferric chloride, which soon turns green and then yellow. When heated with hydriodic acid it gives pyrocatechol, and when distilled with zinc dust, anisol. (Write the equations.) The carbonate  $\text{OC}(\text{O.C}_6\text{H}_4.\text{OCH}_3)_2$  and some other derivatives have been recommended as remedies for tuberculosis.

**NOTE FOR STUDENT.** — How can guaiacol carbonate be made? How is diethyl carbonate made?

Guaiacol is used in making vanillin (426) synthetically and in medicine.

**Veratrol**,  $C_8H_8(OCH_3)_2$ , is the dimethyl ether of pyrocatechol and is made from guaiacol by the action of methyl iodide and alkali. It was first made by the distillation of veratric acid,  $(CH_3O)_2C_6H_3COOH$ , whence the name.

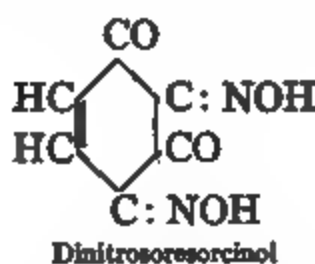
**Resorcinol**, *m*-dihydroxybenzene,  $C_6H_4(OH)_2(m)$ , gets its name from the fact that it was first obtained from the resins, *galbanum* and *asafetida*, by fusion with caustic alkalis. It is made on the large scale by fusing crude sodium benzene-disulphonate with caustic potash. (Write the equation.) This crude salt contains sodium benzene-*p*-sulphonate as well as the *m*-compound. Both are converted into resorcinol by fusion with alkalis, as the *p*-sulphonate undergoes molecular rearrangement by the action of the fused alkali. Resorcinol forms colorless crystals that melt at  $118^\circ$ , and it boils at  $276.5^\circ$ . It is soluble in water, alcohol, ether, and not very soluble in benzene, insoluble in chloroform and carbon bisulphide. Its aqueous solution has an intensely sweet taste. It reduces an ammoniacal solution of silver nitrate and Fehling's solution when heated. With a solution of ferric chloride it gives a dark violet color. It is very readily reduced by boiling its aqueous solution with sodium amalgam to dihydroresorcinol, which acts like a tautomeric substance (see phloroglucinol, 389) : —



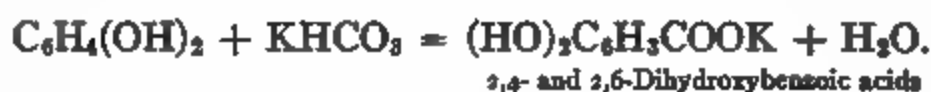
Dihydroresorcinol is a strong acid, as it decomposes carbonates, forming salts (influence of the double bond and of the carbonyl group). It also reacts as a diketone, forming a di-oxime with hydroxylamine. (Write the equations.)

NOTE FOR STUDENT. — Notice the ease with which resorcinol is reduced by nascent hydrogen to a derivative of cyclohexane. From the first formula given for dihydroresorcinol what would it give with bromine? It acts like an unsaturated compound.

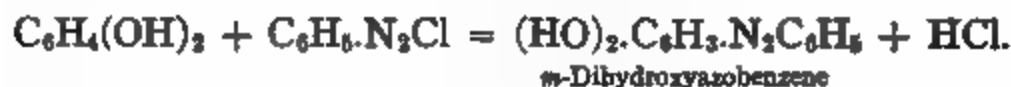
Resorcinol is extremely readily acted upon by reagents, *e.g.*, with bromine water it gives a precipitate of 2,4,6-tribromoresorcinol and with nitric acid 2,4,6-trinitroresorcinol (styphnic acid), both of which act as dibasic acids (compare with picric acid). With nitrous acid it gives 2,4-dinitrosoresorcinol



which is a quinone dioxime (compare with nitrosophenol). It is used as a dye under the name, *Fast green O*. Carboxylic acids of resorcinol are formed by simply boiling its aqueous solution with potassium bicarbonate: —



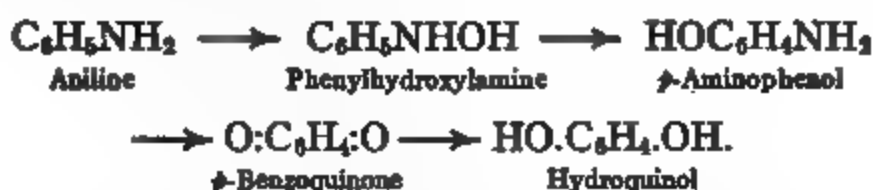
Like *m*-phenylenediamine (345) resorcinol reacts readily with benzenediazonium salts to form azo compounds. In alkaline solution it gives *m*-dihydroxyazobenzene: —



This is used to color alcoholic lacquers and fats under the name of *Sudan G*. Resorcinol when fused with phthalic anhydride gives fluorescein (475), and this reaction is used as a test both for resorcinol and for phthalic acid (415). Neither pyrocatechol nor hydroquinol gives fluorescein with phthalic anhydride. When heated with sodium nitrite, resorcinol is converted into a blue dye, called *Lacmoid* from its resemblance to litmus, as its solution is turned blue by alkalies and red by acids. It is used as an indicator in acidimetry and alkalimetry.

Resorcinol is used in the manufacture of fluorescein and other dyestuffs.

Hydroquinol, *p*-dihydroxybenzene,  $C_6H_4(OH)_2$ , was first obtained by the distillation of quinic acid, whence the name. It is sometimes found in plants, as *arbutin*, a glucoside, which yields hydroquinol on hydrolysis. It is made on the large scale by oxidizing aniline with sodium bichromate and sulphuric acid to *p*-benzoquinone (431) and then reducing this to hydroquinol by means of sulphur dioxide.



It crystallizes from water in colorless, hexagonal prisms which melt at  $169^\circ$ – $170^\circ$  and have a sweet taste. It is easily soluble in alcohol, ether and hot water. The alkaline solution soon turns brown in the air, due to oxidation. It reduces an ammoniacal solution of silver nitrate on warming, and Fehling's solution in the cold. Oxidizing agents convert it into *p*-benzoquinone (431), and this reaction distinguishes it from its two isomers. It has also been obtained by fusing *p*-iodophenol with caustic potash, and, together with phenol and pyrocatechol, by oxidizing benzene with hydrogen peroxide in the presence of iron salts.

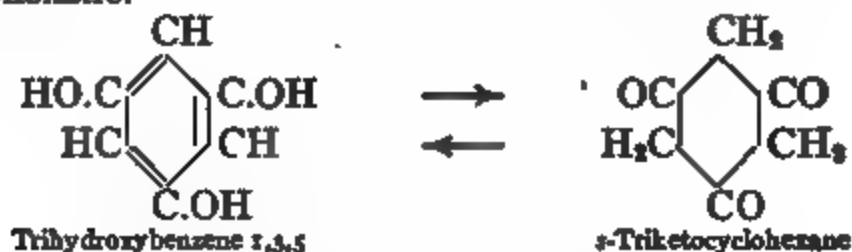
NOTE FOR STUDENT. — What reactions used in the preparation of hydroquinol prove that it is a para compound?

It is used in photography as a developer and also in the manufacture of intermediates (quinizarin, etc.).

Orcinol, *s*-dihydroxytoluene,  $H_3C.C_6H_3(OH)_2$ , 1,3,5, is found in several lichens and results from the fusion of aloes with alkalis. It has been made synthetically from 1,3,5-chlorotoluenesulphonic acid by fusing with caustic soda, which proves its structure. In this reaction the chlorine as well as the sulphonic acid group is replaced by hydroxyl. Orcinol crystallizes with a molecule of water in colorless, monoclinic prisms which rapidly turn red in the air due to oxidation. They are readily

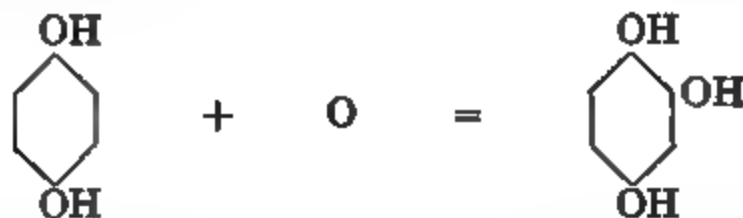


hydroxylamine, however, it gives a trioxime,  $C_6H_3(NO)_3$ , a derivative of cyclohexane. This reaction shows that phloroglucinol contains three carbonyl groups, *i.e.*, that it is *s*-triketocyclohexane.



It will be seen that the second formula is derived from the first by the migration of the hydrogen atoms of the hydroxyl groups to the carbon atoms, and the elimination of the three double bonds. Phloroglucinol has no technical application. It is used to determine the amount of pentosans in plants. When substances containing pentosans are boiled with hydrochloric acid they give furfural (or methyl furfural, 318) which combines with phloroglucinol to form an insoluble compound. From the amount of this compound formed the amount of pentosans present can be calculated. Phloroglucinol is also used to determine the presence of wood pulp in paper. Such paper gives a purplish red color when treated with a solution of phloroglucinol containing hydrochloric acid.

Hydroxyhydroquinol, *u*-trihydroxybenzene,  $C_6H_3(OH)_3$ -1,2,4, is formed by fusing hydroquinone with caustic alkalies in the air:—



Its triacetate,  $C_6H_3(OCOCH_3)_3$ , is formed by heating *p*-benzoquinone (431) and acetic anhydride with a small amount of sulphuric acid. When hydrolyzed with hydrochloric acid this gives hydroxyhydroquinol. It crystallizes in monoclinic leaflets melting at  $140.5^\circ$ .

NOTE FOR STUDENT. — How many monohydroxyhydroquinols are possible and known?

## AROMATIC ALCOHOLS, ALDEHYDES, AND KETONES

The phenols resemble the tertiary alcohols of the paraffin series in some respects, but differ from them in others. Aromatic alcohols, which are completely analogous to the alcohols of the paraffin series, are also known. The simplest of these is benzyl alcohol,  $C_6H_5.CH_2OH$ , or phenylmethyl alcohol (phenylcarbinol), isomeric with the cresols. This is a primary alcohol, as it yields benzoic aldehyde and benzoic acid when oxidized: —



Secondary alcohols, such as diphenylcarbinol,  $(C_6H_5)_2.CHOH$ , formed by the reduction of benzophenone,  $C_6H_5.CO.C_6H_5$  (diphenyl ketone), and tertiary alcohols like triphenylcarbinol,  $(C_6H_5)_3C.OH$ , are also known. The aromatic alcohols are all derivatives of the alcohols of the paraffin series.

**Benzyl alcohol**,  $C_6H_5.CH_2OH$ , is found in the oil of tuberose, ylang-ylang, cloves, and cassia flowers, and in the form of the acetate, benzoate, or salicylate in the oils of tuberose, ylang-ylang, hyacinth, jasmine, gardenia, and in Peru and Tolu balsam. It has been known as a constituent of these two balsams for a long time, but it is only since its discovery in the essential oils of the flowers used in perfumery that its importance has been realized and that it has been manufactured on the large scale. Lately it has come into prominence in medicine. For use in the manufacture of perfumes it is made from benzaldehyde (394) by the action of concentrated solutions of the alkalis: —



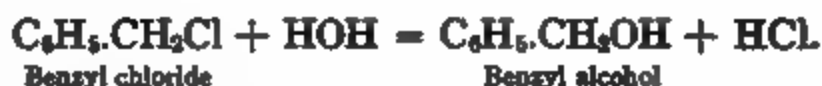
A similar reaction takes place with formaldehyde: —



It will be seen from these reactions that one molecule of the aldehyde oxidizes another molecule to the acid and is itself

reduced to the alcohol. Benzaldehyde is the phenyl derivative of formaldehyde.

Benzyl alcohol is also made on the large scale from benzyl chloride (336) by boiling it with water and freshly precipitated lead oxide:—



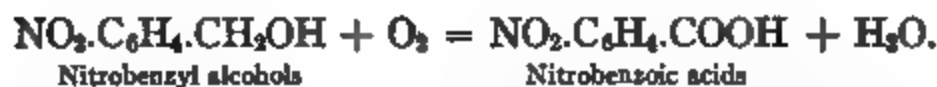
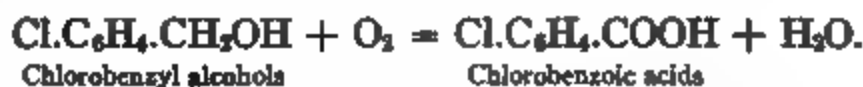
The benzyl alcohol manufactured in this way is apt to contain chlorine compounds which give the alcohol a disagreeable odor and render it unfit for use in perfumery. Benzyl alcohol is a colorless liquid. It has a faint aromatic odor when pure, but soon acquires the odor of oil of bitter almonds on standing in the air in consequence of the formation of some benzaldehyde by oxidation. It boils at 205.5°–206°, and is readily soluble in organic solvents. It is not very soluble in water (1 vol. in 35 of water).

Benzyl alcohol is the phenyl derivative of methyl alcohol and hence is completely analogous to that alcohol in its reactions; *e.g.*, it gives esters with acids, such as benzyl chloride and bromide (336) and benzyl acetate with acetic anhydride. (Write the equations.) It also forms ethers, of which the methyl ether,  $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_3$  (made from benzyl chloride and sodium methylate), and the benzyl ether,  $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$ , are examples.

NOTE FOR THE STUDENT.—What would benzyl alcohol give when treated with sodium? What would this product give when treated with benzyl chloride?

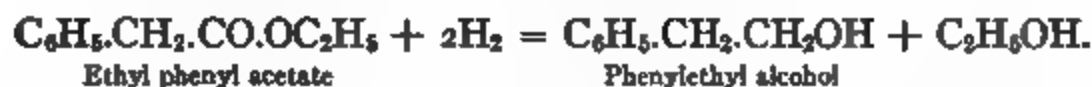
It differs from the cresols in being insoluble in solutions of the alkalies and also in the products which it gives on oxidation. Benzoic aldehyde and benzoic acid are formed from benzyl alcohol by oxidation, while the cresols give the hydroxybenzoic acids (420). Substitution products, such as chlorobenzyl alcohols,  $\text{Cl.C}_6\text{H}_4\text{CH}_2\text{OH}$ , nitrobenzyl alcohols,  $\text{NO}_2\text{.C}_6\text{H}_4\text{CH}_2\text{OH}$ , etc., cannot be made by direct treatment of the alcohol with chlorine or nitric acid, as these reagents

oxidize the alcohol. They are made from the chlorotoluenes,  $\text{Cl.C}_6\text{H}_4.\text{CH}_3$ , or the nitrotoluenes,  $\text{NO}_2.\text{C}_6\text{H}_4.\text{CH}_3$ , by chlorination at the boiling point and the conversion of the chlorobenzyl chlorides,  $\text{Cl.C}_6\text{H}_4.\text{CH}_2\text{Cl}$ , or nitrobenzyl chlorides,  $\text{NO}_2.\text{C}_6\text{H}_4.\text{CH}_2\text{Cl}$ , into the corresponding alcohols by boiling with water. (Write the equations.) These substituted benzyl alcohols are converted into the corresponding benzoic acids by oxidation :—

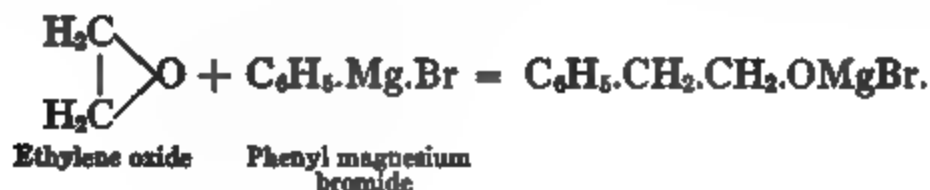


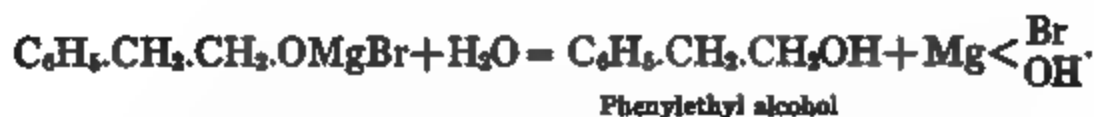
Homologues of benzyl alcohol such as  $\alpha$ -phenylethyl alcohol,  $\text{C}_6\text{H}_5.\text{CHOH}.\text{CH}_3$ , and  $\beta$ -phenylethyl alcohol,  $\text{C}_6\text{H}_5.\text{CH}_2\text{CH}_2\text{OH}$ , one a secondary and the other a primary alcohol, are well known. Homologues are also known, derivatives of the xylenes, cumene, mesitylene, etc., in the same way that benzyl alcohol is derived from toluene, such as tolyl carbinol,  $\text{H}_3\text{C.C}_6\text{H}_4.\text{CH}_2\text{OH}$ , which is known in three forms, ortho-, meta-, and para-, and cuminyl alcohol, *p*-isopropylbenzyl alcohol,  $\text{C}_3\text{H}_7.\text{C}_6\text{H}_4.\text{CH}_2\text{OH}(p)$ , made by reducing cuminol,  $\text{C}_3\text{H}_7.\text{C}_6\text{H}_4.\text{CHO}(p)$ , an aldehyde found in the oil of cumin (398).

Phenylethyl alcohol,  $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}_2\text{OH}$ , occurs in the attar of roses and in neroli oil both in the free state and combined with benzoic acid and with phenylacetic acid in the form of esters. It is made on the large scale in France by the reduction of ethyl phenyl acetate with sodium and absolute alcohol :—



In this country it is made commercially by the Grignard reaction from ethylene oxide and phenylmagnesium bromide in ether solution :—

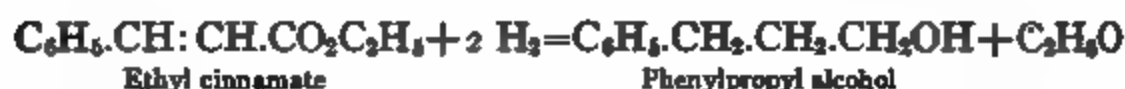




### Phenylethyl alcohol

Phenylethyl alcohol is a colorless liquid boiling at  $220^{\circ}$ – $222^{\circ}$  (740 mm.), having a faint aromatic odor, readily soluble in all the ordinary organic solvents and somewhat soluble in water (1 in 60). It is readily oxidized, even by the air, to phenylacetic aldehyde and hence soon acquires the hyacinth odor of that substance. Chromic acid oxidizes it to phenylacetic aldehyde and phenylacetic acid. It is used in the manufacture of perfumes.

**Phenylpropyl alcohol**,  $C_6H_5.CH_2.CH_2.CH_2OH$ , is found as the ester of cinnamic acid in Sumatra benzoës, in *Styrax* and in other balsams and resins. It is made synthetically by the reduction of ethyl cinnamate with sodium and absolute alcohol :—



### Ethyl cinnamate

### Phenylpropyl alcohol

It is a colorless liquid having an odor somewhat similar to the hyacinth and boiling at 235°. Oxidized with chromic acid it gives hydrocinnamic acid. It is used in the manufacture of perfumes.

## AROMATIC ALDEHYDES

The aromatic aldehydes resemble the aliphatic aldehydes. They result from the oxidation of the *primary aromatic* alcohols, and give these alcohols on reduction. The simplest and most important is the oil of bitter almonds or benzoic aldehyde,  $C_6H_5.CHO$ .

Oil of bitter almonds, benzaldehyde,  $C_6H_5.CHO$ , as its name indicates was first obtained from bitter almonds in which it occurs as amygdalin, a glucoside (528). This is also present in cherry kernels and in cherry-laurel leaves. It is hydrolyzed by *emulsin*, an enzyme present in the bitter almonds, or by dilute mineral acids, into benzoic aldehyde, hydrocyanic acid and glucose : —



### Assessment

### Benzole aldehyde

**Chronic**

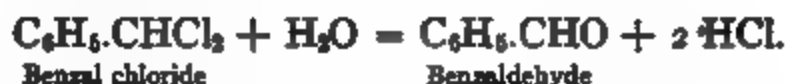
The natural oil of bitter almonds, therefore, contains hydrocyanic acid and is poisonous. Benzaldehyde was first made artificially by oxidation of benzyl alcohol. It has also been made by other methods used in the preparation of aldehydes, e.g. by the distillation of a mixture of calcium benzoate and formate:—



By reducing benzoyl chloride (404) with nascent hydrogen:



and by heating benzal chloride (337) with water in the presence of small amounts of iron or iron salts:—



**NOTE FOR THE STUDENT.** — Show how acetic aldehyde can be made by methods analogous to those given above. What is the action of caustic alkalis on acetic aldehyde and on benzoic aldehyde?

On the large scale benzaldehyde is made from toluene by direct oxidation. Toluene and 65 per cent sulphuric acid are thoroughly stirred while finely powdered manganese dioxide is added, the temperature being kept at 40°. After the reaction is over, benzaldehyde and unchanged toluene are driven over by steam:—



Another method involves the conversion of the toluene into a mixture of benzal chloride and benzotrichloride by the action of chlorine at the boiling point of toluene, and the heating of this product with water in the presence of small amounts of iron or iron salts to 90°–95°. The hydrochloric acid formed in the reaction (see above) is very pure and is collected in water and utilized. After the reaction is over, milk of lime is added and the benzaldehyde removed by steam distillation. After fil-

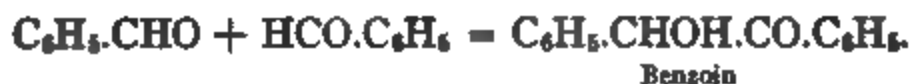
tration of the residue the benzoic acid present in the filtrate in the form of the calcium salt, is recovered by the addition of hydrochloric acid. The benzaldehyde made in this way usually contains small quantities of chlorobenzaldehyde, which comes from a small amount of chlorobenzal chloride unavoidably formed in the chlorination of toluene. When a chlorine-free benzaldehyde is required, as in the manufacture of perfumes, it is manufactured by the direct oxidation of toluene. Benzyl chloride can be converted into benzaldehyde by boiling it with an aqueous solution of lead nitrate:—



In this reaction benzyl alcohol is first formed and is then converted into the aldehyde by the nitric acid set free. (Write the equation.) This method was used at one time for the manufacture of benzaldehyde. The crude benzaldehyde is purified by treating it with aqueous sulphurous acid which dissolves the benzaldehyde (forming a compound with the sulphurous acid soluble in water) leaving the impurities. When this solution is boiled sulphur dioxide is given off and is recovered and used over again, and the pure benzaldehyde is set free.

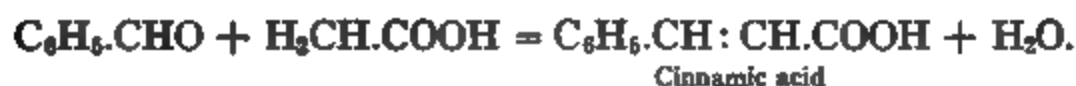
Benzaldehyde is a liquid having the odor of bitter almonds. It melts at  $26^\circ$  and boils at  $179.1^\circ$ . It is difficultly soluble in water (1 part in 600) but very readily soluble in alcohol and ether. It is not poisonous. Like the aliphatic aldehydes it is very readily oxidized even by the oxygen of the air (especially in the sunlight) forming benzoic acid. It reduces an ammoniacal solution of silver nitrate; forms an addition product with sodium bisulphite; combines with hydrogen to form benzyl alcohol, with ammonia and with hydrocyanic acid. With hydroxylamine it gives an oxime (109) and with phenylhydrazine a phenylhydrazone, melting at  $152^\circ$ . When treated with hydrazine sulphate it gives *benzylideneazine*,  $\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{N}=\text{CH}\cdot\text{C}_6\text{H}_5$ , which melts at  $93^\circ$ . With phosphorus pentachloride it gives benzal chloride. (Write all the equations representing these transformations.) Benzaldehyde undergoes condensation (see

aldol condensation), when boiled with an alcoholic solution of potassium cyanide, forming *benzoin*:—



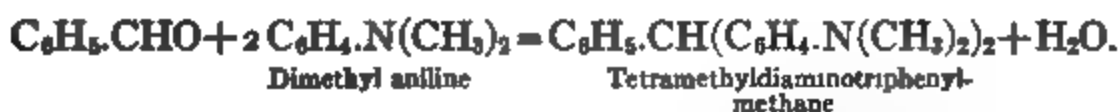
Benzoin is a ketone alcohol, as it takes up hydrogen, forming *hydrobenzoin*,  $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CHOH}\cdot\text{C}_6\text{H}_5$ , and on oxidation gives *benzil*,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , a diketone. Benzoin contains the group  $\text{—CHOH}\cdot\text{CO—}$  characteristic of the sugars. Like the sugars it reduces Fehling's solution and gives a phenylosazone with phenylhydrazine. (Write the equations.)

When heated with the sodium salts of the fatty acids and acetic anhydride, benzaldehyde gives unsaturated acids:—



This reaction (which is called Perkin's synthesis) is supposed to be preceded by the formation of the addition product,  $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{COONa}$  (aldol condensation) from which the acetic anhydride splits off water to give cinnamic acid. Benzaldehyde also reacts in a similar manner with primary aromatic amines. Thus, with aniline it first gives the addition product,  $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{NHC}_6\text{H}_5$ , which then gives *benzylideneaniline*,  $\text{C}_6\text{H}_5\cdot\text{CH}=\text{NC}_6\text{H}_5$ , by the loss of water.

With tertiary aromatic amines benzaldehyde combines very readily, giving substituted amino derivatives of triphenylmethane (463):—



Like other benzene derivatives benzaldehyde can be nitrated and sulphonated. The meta products are the ones formed in largest quantity by the direct action of nitric or sulphuric acid. When chlorinated at the boiling point the chlorine goes into the side chain with the formation of benzoyl chloride,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{Cl}$  (404).



Benzaldehyde is used in the manufacture of the triphenylmethane dyes (malachite green, etc.) and in the manufacture of perfumes. Over 702,000 pounds were made in the United States in 1920.

**Phenylacetic aldehyde**,  $C_6H_5.CH_2.CHO$ , has the odor of hyacinth and is used in the manufacture of perfumes. It is made from cinnamic acid by treating it with hypochlorous acid:—



### Cinnamic acid

### Phenyl- $\alpha$ -chlorolactic acid

This product when heated with dilute sulphuric acid gives phenylacetic aldehyde:—



### Phenyl- $\alpha$ -chlorolactic acid

### Phenylacetic aldehyde

It is a colorless fluid, which colors the skin yellow. It boils at 75° (5 mm. pressure), polymerizes readily, and is easily oxidized to phenylacetic acid. On reduction it gives phenylethyl alcohol,  $C_6H_5.CH_2.CH_2OH$ , and it can be made by the oxidation of this alcohol.

**Cuminic aldehyde, cuminol, *p*-isopropylbenzaldehyde,  $C_8H_7.C_6H_4.CHO(p)$ ,** occurs together with cymene in the oil of cumin, whence the name. It has a pleasant aromatic odor, boils at  $232^\circ$  and resembles benzaldehyde closely in its properties. Dilute nitric acid oxidizes it to cuminic acid (*p*-isopropylbenzoic acid) while chromic acid converts it into terephthalic acid. Nascent hydrogen reduces it to cuminyl alcohol,  $C_8H_7.C_6H_4.CH_2OH(p)$ , and distillation with zinc dust gives cymene (*p*-isopropylmethylbenzene). (Write all the equations.)

**Benzaldoximes,  $C_6H_5.CH:N.OH$ .** — Hydroxylamine reacts with benzoic aldehyde forming benz-anti-aldoxime:—

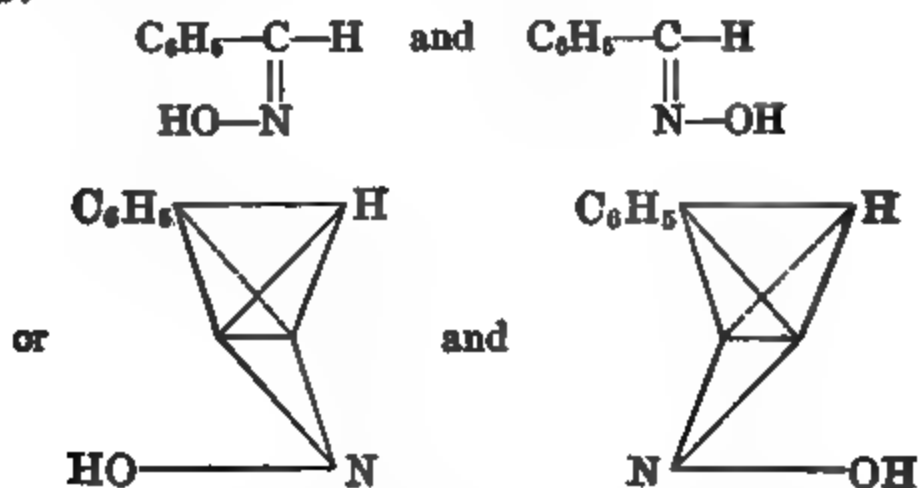


This appears first as an oil, but when purified it forms long, lustrous prisms, melting at  $35^{\circ}$ .

When hydrochloric acid gas is conducted into an ether solution of the above oxime, a hydrochloride is precipitated, and

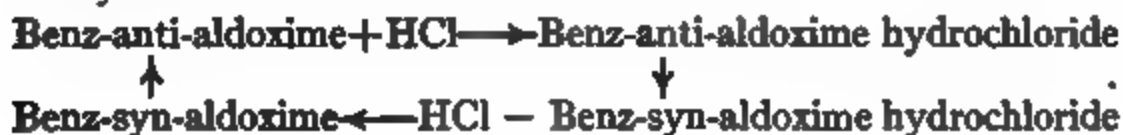
when this is treated with sodium carbonate, benz-syn-aldoxime, isomeric with the above, is obtained. This crystallizes from ether in thin, lustrous needles, and melts, when rapidly heated, at  $125^{\circ}$ . By long-continued heating, however, it is converted into the oxime, melting at  $35^{\circ}$ .

These two oximes are stereoisomeric. In terms of the conceptions of stereochemistry they are represented by the formulas:—



[For an explanation of the significance of these space formulas, especially as far as the nitrogen atom is concerned, see 356.]

The one with the hydrogen atom and the hydroxyl on opposite sides of the plane passing through the doubly bound carbon and nitrogen atoms is called *benz-anti-aldoxime*; the one with the hydrogen atom and the hydroxyl on the same side is called *benz-syn-aldoxime*. The one that melts at  $125^{\circ}$  loses water and forms phenyl cyanide or benzonitril,  $\text{C}_6\text{H}_5\text{CN}$ , when heated with acetic anhydride. The other gives an acetate. The one that loses water and yields the nitril when heated with acetic anhydride is the syn-aldoxime, as in this form the hydrogen and hydroxyl are so situated that they can unite to form water, whereas this is not the case in the anti form. According to this the stable form, the one most easily obtained, is the anti oxime. The following scheme shows how the anti can be converted into the syn oxime and *vice versa*:—



## AROMATIC KETONES

These are of two kinds, the mixed ketones, of which acetophenone (methylphenyl ketone),  $C_6H_5.CO.CH_3$ , is the simplest example, and the aromatic ketones, such as benzophenone (diphenylketone),  $C_6H_5.CO.C_6H_5$ .

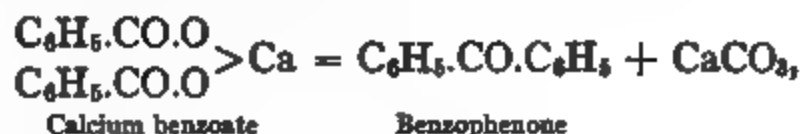
Acetophenone,  $C_6H_5.CO.CH_3$ , is formed from benzene and acetyl chloride in the presence of aluminium chloride (Friedel and Crafts reaction):—



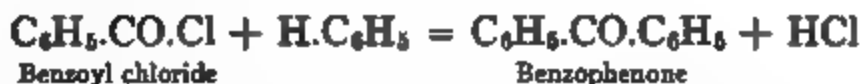
It forms crystals that melt at  $20.5^\circ$  and it boils at  $202^\circ$ . It is present in coal tar. It has an agreeable odor, is only slightly soluble in water and is volatile with steam. It shows all the reactions characteristic of the aliphatic ketones. It was formerly used as a soporific under the name *Hypnone*.

NOTE FOR THE STUDENT. — Give the reactions of acetophenone with hydroxylamine, with phenylhydrazine and with semicarbazide. What does acetophenone give when reduced with nascent hydrogen?

Benzophenone, diphenylketone,  $C_6H_5.CO.C_6H_5$ , is formed when calcium benzoate is distilled:—



or by the action of benzoyl chloride on benzene in the presence of aluminium chloride:—

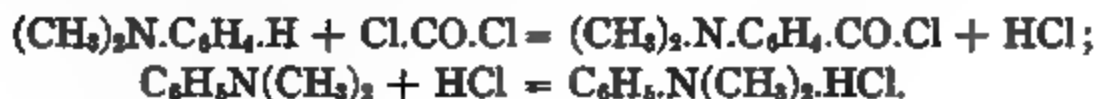


It is dimorphous. The stable modification melts at  $49^\circ$ . When distilled it gives the unstable modification, melting at  $26^\circ$ , which gradually changes (more rapidly on the addition of a crystal of the stable form) to the stable modification. It boils at  $305.7^\circ$  (754 mm.), is insoluble in water, easily soluble in alcohol, ether, and in glacial acetic acid. It acts like the aliphatic ketones, e.g., it gives an oxime melting at  $140^\circ$  and a phenylhydrazone melting at  $105^\circ$ .

One of the derivatives of benzophenone, *Michler's ketone*, *p-p*-tetramethyldiaminobenzophenone,



is of great importance in the manufacture of the triphenylmethane dyes. It is made by conducting phosgene,  $O=C=Cl_2$ , into dimethylaniline until the increase in weight shows that a half molecule of the gas has been absorbed. The crystal mass formed consists of dimethylaminobenzoyl chloride and dimethylaniline hydrochloride:—



This mixture is heated for some time on the water bath in a closed vessel until the reaction is complete:—



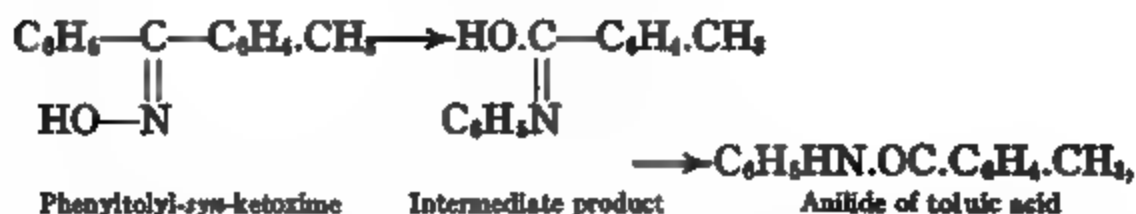
A solution of sodium hydroxide is then added to neutralize the hydrochloric acid, and the unchanged dimethylaniline is removed by distillation in steam. The ketone is purified by dissolving in hydrochloric acid, filtering the solution, and precipitating it with sodium hydroxide. If necessary it is further purified by crystallization from alcohol. It crystallizes in almost colorless leaflets that melt at  $174^\circ$  and are readily soluble in alcohol and ether. On reduction it gives tetramethyldiaminobenzhydrol,  $((CH_3)_2NC_6H_4)_2CHOH$ , *Michler's hydrol*.

The tetraethyl compound,  $(C_2H_5)_2N.C_6H_4.CO.C_6H_4.N(C_2H_5)_2$ , is made in a similar manner from diethylaniline and is used in the manufacture of dyes (light blue, alkali violet 6B, etc.)

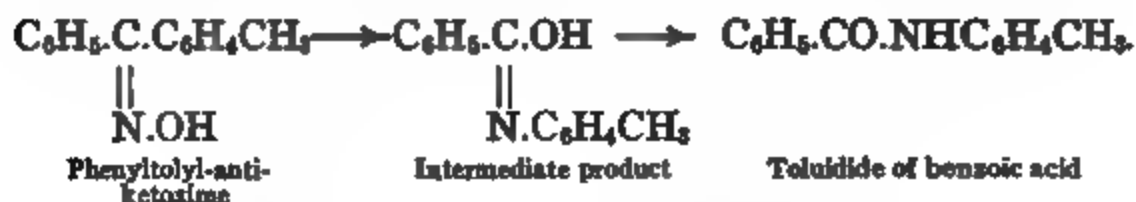
Mixed aromatic ketones, such as phenyltolyl ketone,  $C_6H_5.CO.C_6H_4CH_3$ , give stereoisomeric ketoximes. The configuration of these isomers is determined from the products formed in the Beckmann rearrangement<sup>1</sup>, brought about by sulphuric acid, phosphorus pentachloride, etc. In this molecular

<sup>1</sup> See *Stereochemistry*, by A. W. Stewart, 2d Ed. 1919, page 135.

rearrangement of the ketoximes, the hydroxyl group and aliphyl group on the same side of the plane passing through the doubly bound carbon and nitrogen atoms, exchange places, thus:—



and this intermediate product goes over to the more stable substituted amide of the acid as shown above and below:



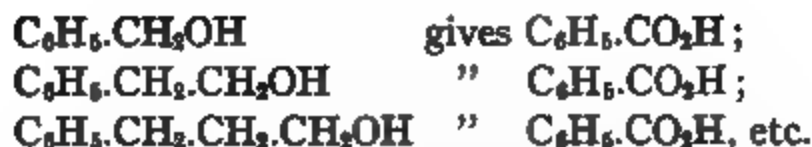
### ACIDS OF THE BENZENE SERIES

The simplest of these acids is benzoic acid, which bears to benzene the same relation that acetic acid bears to marsh gas. It is the carboxyl derivative of benzene. The homologous acids are carboxyl derivatives of the homologous hydrocarbons. There are monobasic, dibasic, tribasic, and even hexabasic acids.

#### MONOBASIC ACIDS, $\text{C}_n\text{H}_{2n-2}\text{O}_2$

**Benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$ .**—Benzoic acid occurs in gum benzoin, in the balsams of Peru and Tolu, in cranberries, and in combination with aminoacetic acid or glycine as hippuric acid (410) in the urine of herbivorous animals. It is present in coal tar. It can be made in many ways, the most important of which are given below:—

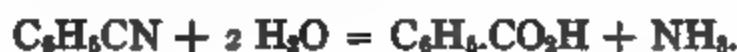
1. By oxidation of benzyl alcohol or any alcohol which is a phenyl derivative of an alcohol of the methyl alcohol series. The common condition in all these alcohols is the presence of the difficultly oxidizable residue,  $\text{C}_6\text{H}_5$ , in combination with an easily oxidizable residue of an alcohol of the marsh gas series:—



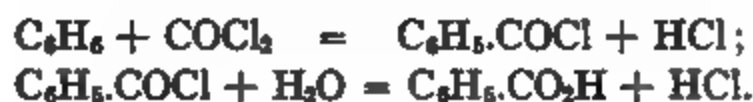
2. By oxidation of benzoic aldehyde, and the aldehydes of the other alcohols referred to in the preceding paragraph.

3. By oxidation of all benzene hydrocarbons which contain but one residue of the marsh gas series. Attention has already been called to this fact (319).

4. By hydrolyzing cyanbenzene (phenyl cyanide, benzonitril) with dilute sulphuric acid:—



5. By treating benzene with carbonyl chloride in the presence of aluminium chloride:—



6. By treating benzene with carbon dioxide in the presence of aluminium chloride:—



This and the preceding method are of special interest from the scientific point of view, for the reason that they clearly show that benzoic acid is the carboxyl derivative of benzene.

NOTE FOR THE STUDENT.—Which of the methods above given are of general application for the preparation of the organic acids? How is benzene made from benzoic acid?

Up to 1877 benzoic acid was made on the large scale from the urine of horses and cattle by hydrolysis of the hippuric acid (410),  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$ , contained therein. This method is no longer used. A small quantity of benzoic acid, principally for medicinal uses, is made at the present time from gum benzoïn. Most of the benzoic acid is now made from toluene either by direct oxidation with manganese dioxide and sulphuric acid or by chlorinating the toluene at the boiling point

to benzotrichloride and heating this with milk of lime and a small amount of iron powder: —



NOTE FOR THE STUDENT. — What does chloroform give when heated with a solution of an alkali? Of what aliphatic compounds are benzotrichloride and benzoic acid derivatives?

The benzoic acid made by the last method generally contains a trace of chlorobenzoic acid due to the presence of a small amount of chlorobenzotrichloride in the benzotrichloride. Considerable benzoic acid is obtained as a by-product in the manufacture of benzaldehyde (396).

Benzoic acid forms lustrous laminae or needles that melt at  $121^\circ$ . It boils at  $250^\circ$ . It is comparatively easily soluble in hot water, but difficultly soluble in cold water. It is volatile with steam, and is purified by steam distillation. Its vapor acts upon the mucous membrane of the respiratory passages, and causes coughing. It sublimes very readily.

Benzoic acid is about 3.3 times as strong as acetic acid, owing to the influence of the negative phenyl group. It is, however, a weaker acid than formic acid. When heated with lime, benzoic acid breaks down, giving benzene and carbon dioxide.

With sodium amalgam and water it yields benzyl alcohol. With hydriodic acid, it gives toluene and hydrogen addition products of toluene.

*Sodium benzoate* is extensively used as a preservative. Over 800,000 lb. were made in the United States in 1920.

The ethereal salts of benzoic acid can be made by any of the general methods used in the preparation of esters (67).

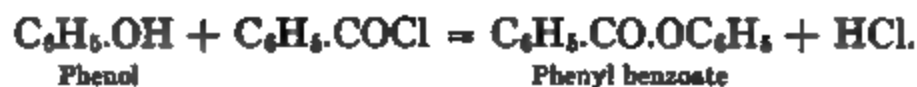
Di-, tetra-, and hexahydro addition products of benzoic acid have been made. Hexahydrobenzoic acid,  $\text{C}_6\text{H}_{11}\text{COOH}$ , is the carboxyl derivative of cyclohexane. It is found in Russian petroleum. It gives cyclohexane when distilled with lime. It has a rancid odor like that of capric acid.

Benzoyl chloride,  $\text{C}_6\text{H}_5.\text{COCl}$ , is made from benzoic acid by the action of phosphorus pentachloride. On the large scale it is made from benzoic aldehyde by treating it with chlorine: —

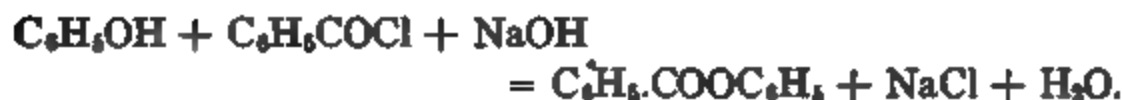


It is more stable than the chlorides of the fatty acids, but undergoes the same kinds of change. It is insoluble in water and is only slowly hydrolyzed by water. It is a colorless liquid, boiling at  $193.9^\circ$ – $194.1^\circ$ , and has a characteristic pungent odor.

Benzoyl chloride when heated with alcohols and phenols, amino and imino compounds acts upon them in the same way that acetyl chloride does, and forms benzoyl compounds:—



When benzoyl chloride is treated with an aqueous solution of a phenol or an alcohol containing sodium hydroxide, it gives a benzoate:—



This Baumann-Schotten reaction, as it is called, furnishes a valuable method for detecting alcoholic or phenolic hydroxyl groups.

Benzamide,  $\text{C}_6\text{H}_5\text{CONH}_2$ , is made by treating benzoyl chloride with ammonia:—



It crystallizes in plates, melting at  $130^\circ$ , and is soluble in hot water. It acts as a weak acid and dissolves in alkalis, as the hydrogen atoms of the amino group are replaceable by metals, owing to the influence of the benzoyl group. When distilled with phosphorus pentoxide benzamide gives benzonitrile:—



Benzanilide,  $\text{C}_6\text{H}_5\text{CO.NH.C}_6\text{H}_5$ , analogous to acetanilide, is made by the action of benzoyl chloride on aniline.



Benzoyl cyanide,  $C_6H_5COCN$ , is made by distilling potassium cyanide and benzoyl chloride:



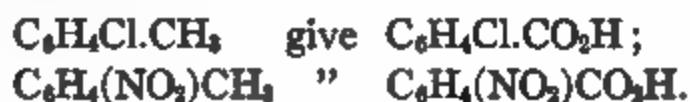
On hydrolysis benzoyl cyanide gives the acid  $C_6H_5.CO.CO_2H$ . This is known as *benzoylformic acid*. It is of interest, for the reason that one of its derivatives is closely related to indigo. (See Isatin, 409.)

#### SUBSTITUTION PRODUCTS OF BENZOIC ACID

Benzoic acid readily yields substitution products when treated with the halogens, and with nitric and sulphuric acids. The products obtained by direct substitution belong to the meta series. Thus, when chlorine acts upon benzoic acid, the main product is *meta-chlorobenzoic acid*; nitric acid gives mainly *meta-nitrobenzoic acid*; and sulphuric acid gives mainly *meta-sulphobenzoic acid*.

NOTE FOR THE STUDENT. — Compare this with the result of the direct action of the same reagents on toluene and on nitrobenzene.

Substituted benzoic acids can be made, also, by oxidizing the corresponding substituted toluenes. Thus, the chlorotoluenes give chlorobenzoic acids; nitrotoluenes give nitrobenzoic acids, etc: —



The three *nitrobenzoic acids* and the corresponding *amino-benzoic acids* may serve as examples of the mono-substitution products.

**Ortho-nitrobenzoic acid,  $NO_2C_6H_4COOH$ .** — Ortho-nitrobenzoic acid is formed, together with a large quantity of the meta acid and some of the para acid, by treating benzoic acid with nitric acid. It is best made by oxidizing ortho-nitrotoluene with potassium permanganate, and by oxidizing ortho-nitrocinnamic acid. It crystallizes in needles, melts at  $147^\circ$ , and has an intensely sweet taste.

**Meta-nitrobenzoic acid**,  $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$ , is the chief product of the action of nitric acid on benzoic acid. It crystallizes in laminae, or plates, and melts at  $140^\circ$  to  $141^\circ$ .

**Para-nitrobenzoic acid**,  $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$ , is best prepared by oxidizing para-nitrotoluene. It crystallizes in laminae, melts at  $238^\circ$ , and is much less soluble in water than the ortho and meta acids.

The nitrobenzoic acids are much stronger acids than benzoic acid, owing to the influence of the nitro group. The ortho acid is the strongest of the three, while the meta and para acids have about the same strength.

The determination of the series to which these three acids belong is effected by transforming them into the amino acids; and these, through the diazonium compounds, into the corresponding hydroxy acids of the formula  $\text{HOC}_6\text{H}_4\text{COOH}$ .

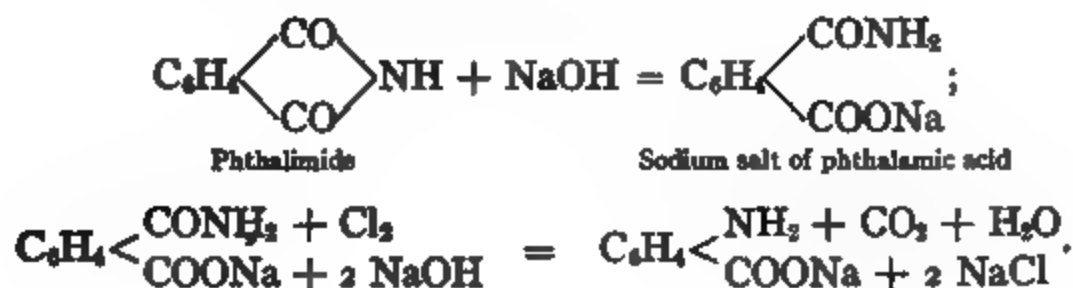
**NOTE FOR THE STUDENT.**— Give the equations representing the reactions involved in passing from toluene to ortho-hydroxybenzoic acid (salicylic acid) by the method above referred to. See below.

In a similar way, lines of connection have been established between the three hydroxy acids and the chloro-, bromo-, and iodobenzoic acids.

**NOTE FOR THE STUDENT.**— What are the reactions?

The three hydroxy acids, on the other hand, have been made by methods that connect them directly with the three dibasic acids of benzene,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ , which, in turn, have been made from the three xylenes.

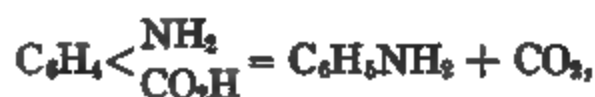
**Anthranilic acid, ortho-aminobenzoic acid,  $\text{H}_2\text{NC}_6\text{H}_4\text{COOH}$ .**— This acid can be made by reducing ortho-nitrobenzoic acid with tin and hydrochloric acid. It is made on the large scale from phthalimide by Hofmann's reaction (257):—



*o*-Nitrotoluene is converted into anthranilic acid by boiling with solutions of alkalis:—



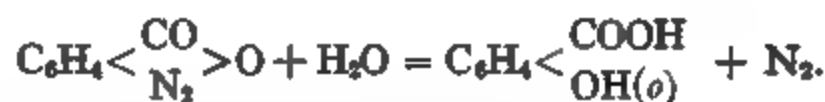
It is also formed by boiling indigo with caustic potash. It has already been stated that indigo yields aniline. Now, as *ortho*-aminobenzoic acid is also obtained, and this breaks down into aniline and carbon dioxide,



it seems probable that the aniline is a secondary product.

Anthranilic acid melts at  $145^\circ$ . It is soluble in water and alcohol, and yields salts with acids and with bases (compare with aminoacetic acid). The methyl ester is a constituent of the oil of orange blossoms, neroli oil, and oil of jasmine. It is made on the large scale from anthranilic acid, and is used in the manufacture of perfumes.

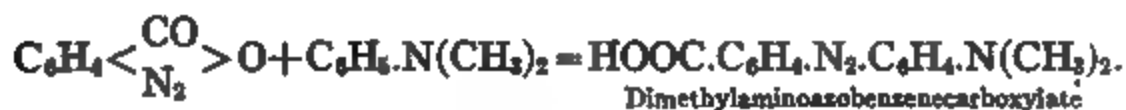
Like other amino acids, anthranilic acid is an inner ammonium salt and should, accordingly, be represented by the formula  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \text{NH}_3 \end{smallmatrix} > \text{O}$ . When it is diazotized it yields an inner diazonium salt of the formula  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \text{N}_2 \end{smallmatrix} > \text{O}$ . When this is boiled with water it yields salicylic acid:—



The solutions of anthranilic acid have a sweet taste and a blue fluorescence which is characteristic of the substance. Anthranilic acid is reduced when treated in solution in amyl alcohol with sodium to hexahydroanthranilic acid, hexahydrobenzoic acid and *n*-pimelic acid,  $\text{HOOC}(\text{CH}_2)_5\text{COOH}$  (157). Anthranilic acid was at one time used in the manufacture of artificial indigo. It is used in the manufacture of azo

dyes, thiosalicylic acid, and of the methyl ester of anthranilic acid.

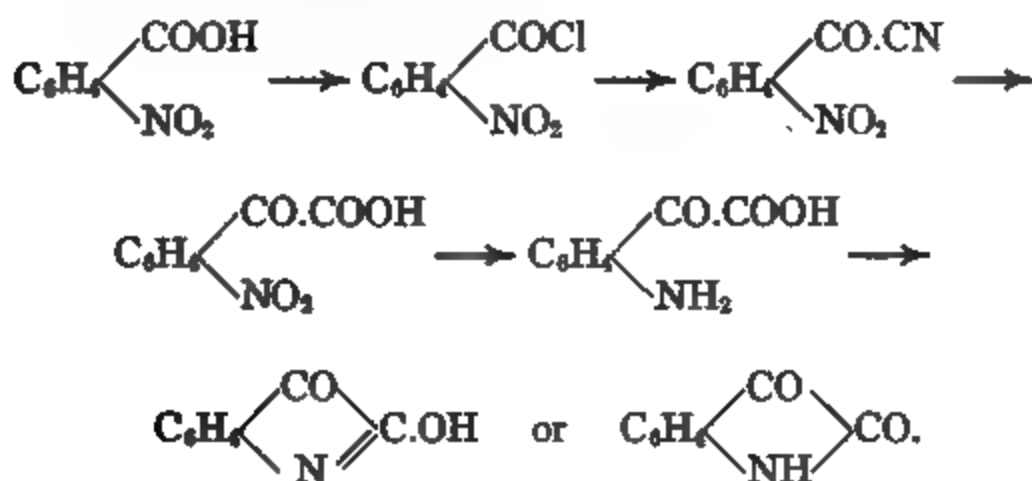
When benzenediazonium carboxylate,  $\text{C}_6\text{H}_5\text{N}_2\text{CO}_2$ , which is completely analogous to benzenediazonium sulphonate (370) is treated with dimethylaniline it forms an azo compound:—



This azo compound is known as *Methyl Red* and is a very valuable indicator in acidimetry and alkalimetry. It is used especially in the Kjeldahl determination of nitrogen.

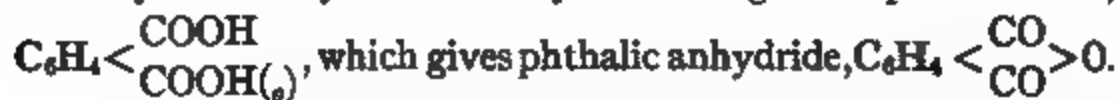
**Isatin**,  $\text{C}_6\text{H}_4\text{N}(\text{CO})_2$ . — Isatin is obtained by the oxidation of indigo, and from ortho-nitrobenzoic acid as follows:—

The nitro acid is converted into the acid chloride, the chloride into the cyanide, and this into the corresponding carboxyl derivative, which is the ortho-nitro derivative of benzoylformic acid. The ortho-nitrobenzoylformic acid is then reduced to the amino compound, and this loses water and gives isatin. The changes are indicated thus:—



The formula given for isatin represents it as an anhydride of ortho-aminobenzoylformic acid. The formation of anhydrides of dibasic acids is a characteristic of ortho compounds. Neither the meta nor para acid gives up water. We shall find that this

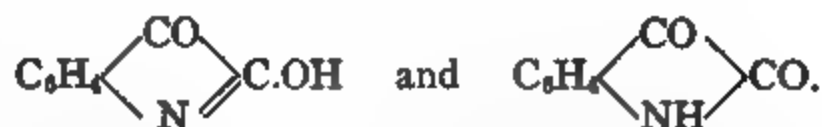
fact is illustrated in the case of the dibasic acids of benzene, the only one that yields an anhydride being ortho-phthalic acid,



This ready formation of anhydrides from ortho compounds, taken together with the fact that the meta and para compounds do not yield anhydrides, is an argument in favor of the view that in the ortho compounds the two substituting groups are actually nearer together than in the meta and para compounds. (See Maleic acid, 293.)

Isatin crystallizes in reddish yellow, monoclinic prisms melting at  $201^\circ$ , sparingly soluble in water, but readily in alcohol. When heated with phosphorus pentachloride it gives isatin chloride,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{C}.\text{Cl}$ , and when this is reduced with zinc dust and acetic acid it gives indigo.

Isatin illustrates the phenomenon of tautomerism (96). Towards some reagents it reacts as though it contained hydroxyl; towards others as though it contained the imino group  $\text{NH}$ , as represented by the two formulas:—



The first of these formulas is known as the *lactim*, the second as the *lactam* formula. The evidence is in favor of the lactam formula for isatin, but derivatives of the lactim formula are also known. Isatin is a pseudo acid (340), as the sodium salt has the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{CONa}.$

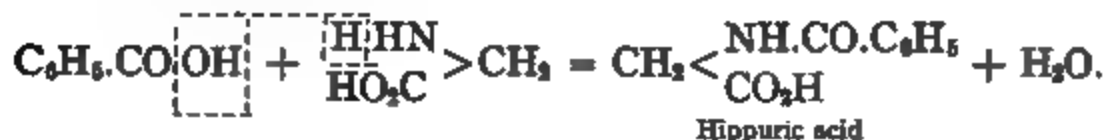
**Meta- and Para-aminobenzoic acids** are made from the corresponding nitro acids by reduction. The ethyl ester of *p*-aminobenzoic acid has anæsthetic properties and is called *anæsthesin*. *Novocaine*, a very valuable local anæsthetic, is the diethylamine derivative of anæsthesin,  $\text{H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{C}_2\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2\text{HCl}$ .

**Hippuric acid**, benzoylaminoacetic acid,  $\text{CH}_2 \begin{array}{c} \text{CO}_2\text{H} \\ \diagdown \quad \diagup \\ \text{NHOC}_6\text{H}_5 \end{array}$ , occurs in the urine of herbivorous animals. A small quantity

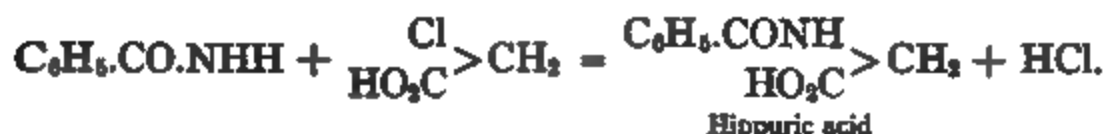
is found in normal human urine. If toluene or benzoic acid is taken with the food, it appears as hippuric acid in the urine, while derivatives of benzoic acid appear as derivatives of hippuric acid.

Hippuric acid has been made synthetically:

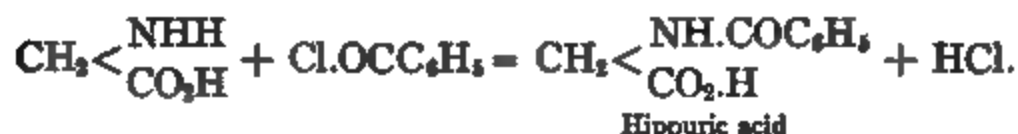
1. By heating glycine with benzoic acid to  $160^{\circ}$ :—



2. By heating benzamide with chloroacetic acid:—

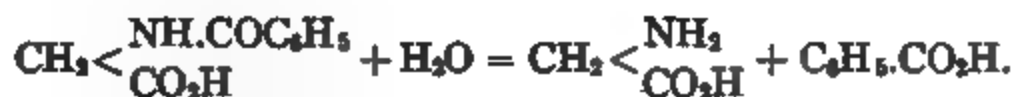


3. By heating glycine with benzoyl chloride:—



Hippuric acid crystallizes from water in long, orthorhombic prisms which melt at  $187^{\circ}$ .

It is hydrolyzed into benzoic acid and glycine by boiling with alkalis, and more readily by boiling with dilute acids:—



NOTE FOR THE STUDENT. — What relation does hippuric acid bear to benzamide? What is the effect of boiling acid amides with alkalis? Write the equation for the hydrolysis of benzamide, and compare it with that for the hydrolysis of hippuric acid.

Sulphobenzoic acids,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{COOH} \\ | \\ \text{SO}_2\text{OH} \end{array}$ . — When sulphuric acid or sulphur trioxide acts upon benzoic acid the principal product is meta-sulphobenzoic acid. The ortho and para acids are made by oxidizing ortho- and para-toluenesulphonic acids:—



*o*-Sulphobenzoic acid when anhydrous melts at  $130^{\circ}$ . It resembles phthalic acid (415) in its reactions. Thus it forms an anhydride, melting at  $129.5^{\circ}$ , and an imide (see below). With phosphorus pentachloride it gives two dichlorides, melting at  $40^{\circ}$  and  $79^{\circ}$ , which have the symmetrical,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO}\cdot\text{Cl} \\ \text{SO}_2\text{Cl} \end{smallmatrix}$ ,

and unsymmetrical,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CCl}_3 \\ \text{SO}_2 \end{smallmatrix} \text{O}$ , formulas (417).

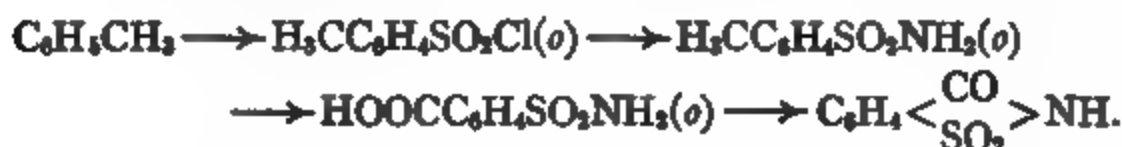
When the anhydride or the chlorides of *o*-sulphobenzoic acid are heated with phenols they give the phenol sulphonphthaleins, which are completely analogous to the phthaleins (472) and are largely used as indicators and in determining hydrogen-ion concentration.

When the amide of *o*-toluenesulphonic acid,  $\text{H}_3\text{CC}_6\text{H}_4\text{SO}_2\text{NH}_2$ , is oxidized with potassium permanganate it gives the potassium salt of *o*-sulphaminobenzoic acid,  $\text{KOCC}_6\text{H}_4\text{SO}_2\text{NH}_2$ . When the solution is acidified the *o*-sulphaminobenzoic acid first formed loses a molecule of water and gives *benzoic sulphinide*,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} > \text{NH}$ , which is the imide of *o*-sulphobenzoic acid, analogous to succinimide,  $\text{C}_2\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{NH}$ .

Benzoic sulphinide has about five hundred times the sweetening power of cane sugar, and in consequence it has come into extensive use as a sweetening agent. It has no food value and is eliminated unchanged from the body by the kidneys. In commerce it is known as *saccharin*. It is a crystallized substance rather difficultly soluble in water, but readily soluble in alcohol and ether. It is soluble in acetone, and crystallizes beautifully from this. It melts at  $223^{\circ}$ – $224^{\circ}$ .

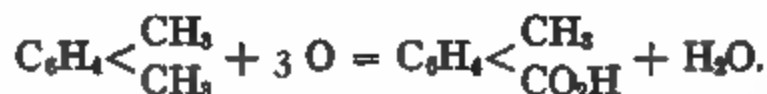
On the large scale benzoic sulphinide is made as follows: Toluene is treated with chlorosulphonic acid, and a mixture of about equal parts of the *p*-toluenesulphonyl chloride and the ortho product is obtained. The ortho chloride is liquid and can be separated from the solid para chloride. When treated with ammonia it gives *o*-toluenesulphonamide. This is con-

verted into the amide of o-sulphobenzoic acid by oxidation with sodium bichromate and sulphuric acid, and by loss of water this gives the sulphinide.

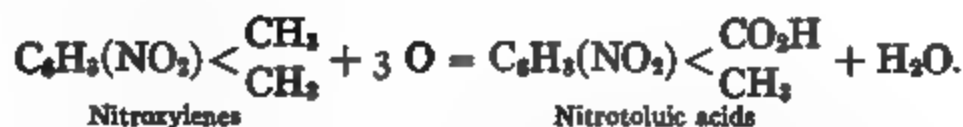


The hydrogen atom of the imino group has acid properties. The sodium salt  $\text{C}_6\text{H}_4\left\langle \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} \right\rangle \text{NNa}$  is soluble in water and is known as *soluble saccharin*. Commercial saccharin contains only a trace of para-sulphaminobenzoic acid. Over half a million pounds of saccharin were produced in the United States in 1919.

**Toluic acids,  $\text{C}_8\text{H}_8\text{O}_2$ .** — There are four acids of this formula known, *viz.*, the three carboxyl derivatives of toluene, in which the carboxyl replaces a hydrogen atom in the benzene ring,  $\text{H}_3\text{CC}_6\text{H}_4\text{COOH}$ , and an acid obtained from toluene by substituting carboxyl for a hydrogen atom of the methyl,  $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{H}$ . *Ortho*-, *meta*-, and *para*-toluic acids are made by oxidizing the corresponding xylenes with nitric acid: —



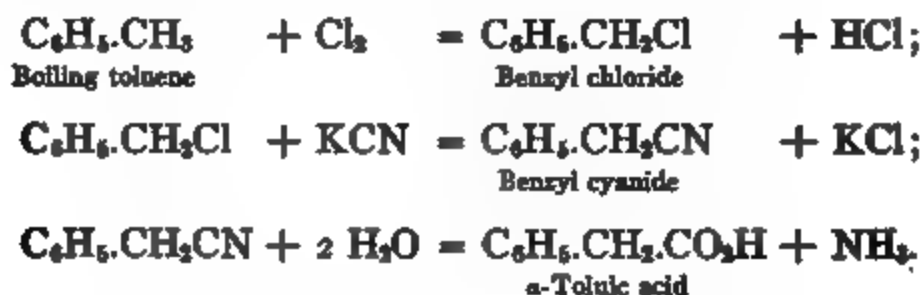
They, as well as their derivatives, of which many are known, have been studied carefully. The substituted toluic acids can be made either by direct treatment of the acids with reagents or by oxidizing substituted xylenes: —



**o-Toluic acid, phenylacetic acid,  $\text{C}_8\text{H}_8\text{CH}_2\text{CO}_2\text{H}$ .** — Just as benzoic acid is regarded as phenylformic acid, so o-toluic acid is phenylacetic acid. It is obtained by reducing mandelic or phenylglycolic acid,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$ , which is formed when amygdalin is treated with hydrochloric acid. It is prepared from toluene by converting it into benzyl chloride, from which



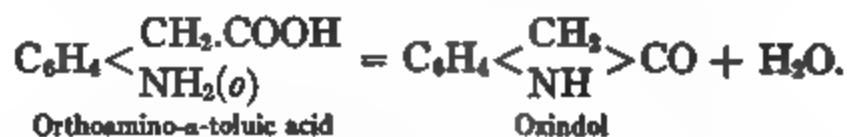
the cyanide is made by boiling with potassium cyanide. The cyanide is then hydrolyzed and yields the acid:—



The acid crystallizes in thin laminæ, and melts at 76.5°.

NOTE FOR THE STUDENT. — What would you expect  $\alpha$ -toluic acid to yield when oxidized? (403.) What would you expect it to yield when distilled with lime? What would you expect the three toluic acids,  $\text{H}_3\text{CC}_6\text{H}_4\text{COOH}$ , to yield by oxidation, and when distilled with lime? (319.)

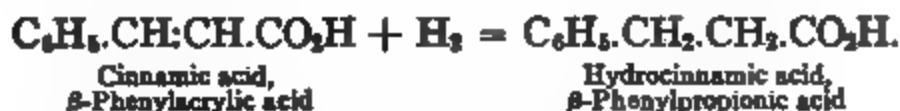
Oxindol,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix}\rangle\text{CO}$ , is obtained by reduction of isatin and of dioxindol (497); and also from *o*-amino- $\alpha$ -toluic acid by loss of water, in the same way that isatin is formed from *o*-aminobenzoylformic acid. It melts at 120°. When  $\alpha$ -toluic acid is treated with nitric acid, the para- and ortho-nitro acids are formed. The latter is reduced by means of tin and hydrochloric acid, when oxindol is at once obtained:—



**Mesitylenic acid**,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{COOH}$ . — This acid has already been referred to as the first product of oxidation of mesitylene. It is the only monobasic acid that has been obtained by the oxidation of mesitylene; and it is the only one possible. By distillation with lime, it yields metaxylene. Further oxidation converts it into uvitic and trimesitic acids (323).

NOTE FOR THE STUDENT. — Of what special significance is the formation of metaxylene from mesitylenic acid? How many monobasic acids does pseudocumene give when oxidized? How many does hemimellitene give? What do these acids give when distilled with lime?

**Hydrocinnamic acid,  $\beta$ -phenylpropionic acid,  $C_6H_5.CH_2.CH_2.CO_2H$ .** — This acid is obtained by treating cinnamic acid with nascent hydrogen: —



It is also made by starting with ethyl benzene,  $C_6H_5.C_2H_5$ , and carrying out the same reactions that are necessary to transform toluene into  $\alpha$ -toluic acid (414). It is a product of the putrefaction of several proteins, such as albumin and fibrin and of the brain substance. It crystallizes from water, in long needles, which melt at  $48^\circ$ . It yields benzoic acid when oxidized with chromic acid, and ethylbenzene when distilled with lime.

**Ortho-aminohydrocinnamic acid,  $H_2NC_6H_4.CH_2CH_2CO_2H$ .** — This acid is prepared from hydrocinnamic acid in the same way that ortho-amino- $\alpha$ -toluic acid is made from  $\alpha$ -toluic acid. It is not known in the free state, but, like the ortho-amino derivatives of benzoylformic and of  $\alpha$ -toluic acids, it loses water, and forms an anhydride, hydrocarbostyryl.

**Hydrocarbostyryl,  $C_6H_4\langle\begin{smallmatrix} C_2H_4 \\ N \end{smallmatrix}\rangle C.OH$ ,** is made by treating ortho-nitrohydrocinnamic acid with tin and hydrochloric acid. It crystallizes in prisms, melting at  $160^\circ$ . It is interesting chiefly for the reason that it is closely related to the important compound *quinoline* (507). When heated with phosphorus pentachloride, hydrocarbostyryl is converted into dichloroquinoline, which gives quinoline on reduction.

#### DIBASIC ACIDS, $C_8H_6-10O_4$

The simplest acids of this group are the three phthalic acids, which are the dicarboxyl derivatives of benzene, belonging to the ortho, meta, and para series.

**Phthalic acid, ortho-phthalic acid,  $C_6H_4\langle\begin{smallmatrix} CO_2H \\ CO_2H(o) \end{smallmatrix}\rangle$ .** — Phthalic acid was the first of the three acids of this composition discovered; and, as it was obtained from naphthalene, it was

named phthalic acid. It is manufactured on the large scale by oxidizing naphthalene by means of concentrated sulphuric acid in the presence of a little mercuric sulphate at a temperature of  $220^{\circ}$ – $300^{\circ}$ . (See equation below.) It can be made from alizarin and purpurin; and from ortho-toluic acid,  $\text{H}_3\text{CC}_6\text{H}_4\text{COOH}(o)$ , by oxidation with potassium permanganate.

Phthalic acid forms orthorhombic crystals, which melt at  $213^{\circ}$  or lower, for, when heated, it breaks down gradually, even below the melting point, into water and the anhydride, which melts at  $131^{\circ}$ . Distilled with lime, it yields benzene; though, by selecting the right proportions, benzoic acid can be obtained:—

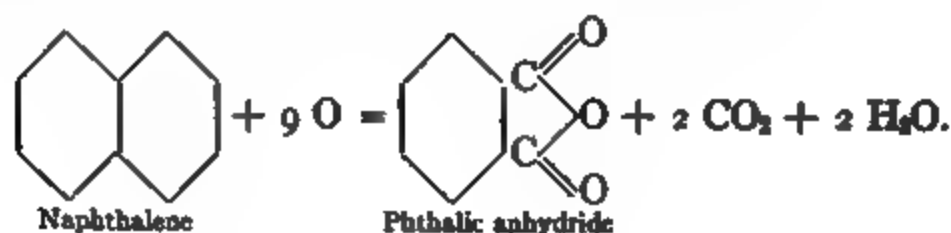


Phthalic acid is a much stronger acid than either of its isomers (compare oxalic acid and its homologues). It is about 20 times as strong as benzoic acid.

By boiling orthoxylenes with nitric acid it yields ortho-toluic acid,  $\text{H}_3\text{CC}_6\text{H}_4\text{COOH}(o)$ , and this is oxidized to phthalic acid by treatment with potassium permanganate.

**Phthalic anhydride**,  $\text{C}_6\text{H}_4\left<\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\right>\text{O}$ , is formed by heating phthalic acid. It forms long needles, which melt at  $131^{\circ}$ . Heated with phenols, it forms the compounds known as *phthalins* (472). On reduction it gives *phthalid*,  $\text{C}_6\text{H}_4\left<\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\right>\text{O}$ . This is the anhydride or lactone of *o*-hydroxymethylbenzoic acid,  $\text{HOCH}_2\text{C}_6\text{H}_4\text{COOH}$ .

Phthalic anhydride is now made in this country on the large scale by passing the vapor of naphthalene and air over a catalyst (vanadium oxide) heated to the proper temperature:—



Nearly 800,000 pounds were made in the United States in 1920 by this method. It is used in the manufacture of the phthalein dyes, of anthraquinone, and of phenolphthalein.

Phthalyl chloride is formed by the action of phosphorus pentachloride on phthalic anhydride. It is known in two forms:

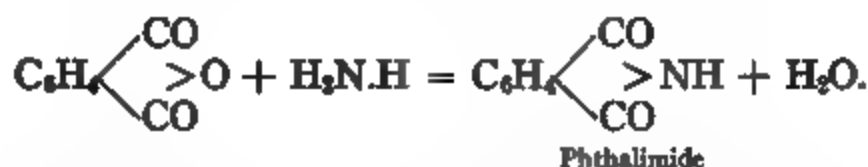


The melting point of 1 is  $15^\circ\text{--}16^\circ$ , that of 2 is  $88^\circ\text{--}89^\circ$ . The two forms are very readily converted into one another; thus, merely warming with aluminium chloride converts the symmetrical (1) into the unsymmetrical chloride (2), while heating on the water bath for several hours transforms the unsymmetrical into the symmetrical chloride.

Phthalic anhydride resembles succinic anhydride (162) closely. Thus, when heated with alcohols it gives the acid phthalates:—



and with ammonia it yields phthalimide:—



*Diethyl phthalate*,  $\text{C}_6\text{H}_4(\text{COOC}_2\text{H}_5)_2$ , made by heating phthalic anhydride with a 3 per cent solution of hydrochloric acid in ethyl alcohol, is used in denaturing alcohol for the manufacture of perfumes, lotions, etc. It is a liquid, boiling at  $295^\circ$ .

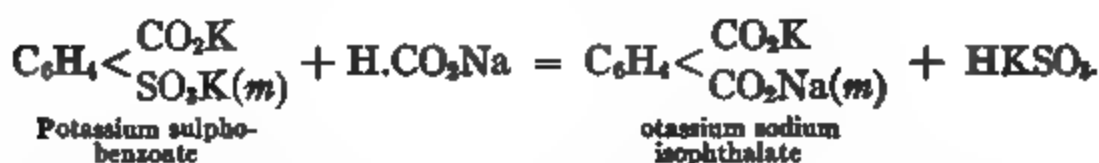
*Potassium acid phthalate*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{COOK} \\ \diagdown \text{COOH} \end{array}$ , is used in making standard solutions in acidimetry and alkalimetry and in determining hydrogen-ion concentration.

*Isophthalic acid, meta-phthalic acid*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO}_2\text{H} \\ \diagdown \text{CO}_2\text{H}(m) \end{array}$ , is formed by oxidizing either metaxylene or meta-toluic acid with chromic

acid; by distilling meta-benzenedisulphonic acid with potassium cyanide, and boiling the resulting dicyanide with a solution of alkali.

**NOTE FOR THE STUDENT.** — Write the equations representing the reactions involved in passing from meta-benzenedisulphonic acid to isophthalic acid. Into which dihydroxybenzene is this same disulphonic acid converted by fusing it with caustic potash?

The acid is formed, further, by heating the potassium salt of meta-sulphobenzoic acid with sodium formate: —

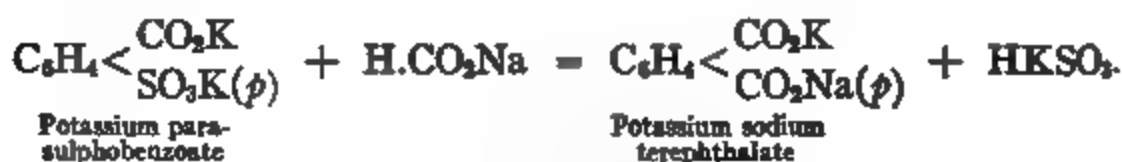


This reaction is of importance, for the reason that the same sulphobenzoic acid, which is thus converted into isophthalic acid, can also be converted into one of the three hydroxybenzoic acids; and thus connection is established between the latter and isophthalic acid and metaxylene.

Isophthalic acid crystallizes in fine needles from water. It melts above  $300^\circ$ , and is not converted into an anhydride.

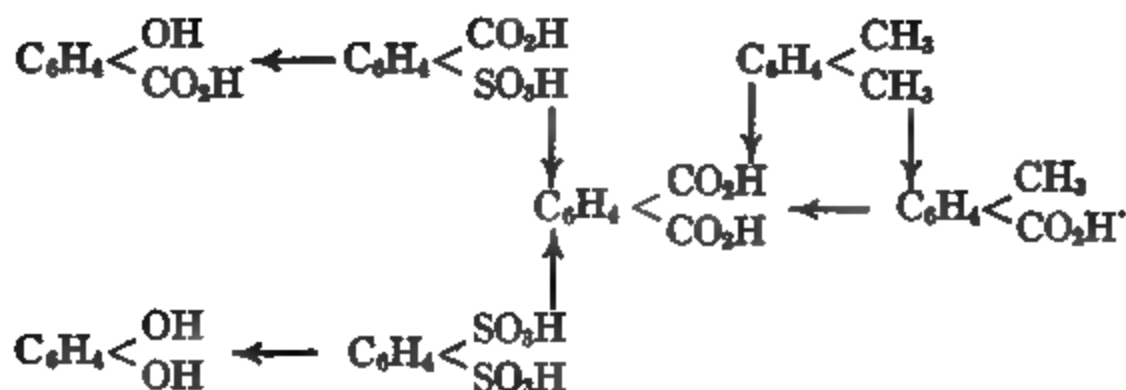
**Terephthalic acid, para-phthalic acid,**  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H}(p) \end{smallmatrix}$ .

Terephthalic acid is formed by oxidation of the oil of turpentine,<sup>1</sup> *p*-cymene, paraxylene, and para-toluic acid; and by heating a mixture of potassium para-sulphobenzoate and sodium formate: —



Para-sulphobenzoic acid is converted into one of the three hydroxybenzoic acids by caustic potash. In the para as well as the meta series, the lines of connection indicated below have been established: —

<sup>1</sup> The prefix *tere* is derived from the Latin *terebinthinus*, turpentine.



Terephthalic acid is a solid that is practically insoluble in water. It sublimes without melting and, like isophthalic acid, yields no anhydride.

### HYDROPHTHALIC ACIDS

Di-, tetra-, and hexa-hydrophthalic acids have been made from all three phthalic acids by reducing them with sodium amalgam. The di- and tetra-hydro acids act like the unsaturated acids, while the hexahydro acids resemble the saturated fatty acids.

### HEXABASIC ACID

**Mellitic acid,  $\text{C}_6(\text{CO}_2\text{H})_6$ .** — This acid occurs in nature in the form of the aluminium salt, as the mineral *honey-stone* or *mellite*. The mineral is rare, and is found in beds of lignite. Mellitic acid has been made by direct oxidation of graphite with potassium permanganate, and by oxidation of hexamethylbenzene,  $\text{C}_6(\text{CH}_3)_6$ . By heating with sodalime it is converted into benzene and carbon dioxide:—



### PHENOL ACIDS, OR HYDROXY ACIDS OF THE BENZENE SERIES

It will be remembered that the alcohol acids or hydroxy acids of the paraffin series form an important class, including such compounds as glycolic, lactic, malic, tartaric, and citric acids. The peculiarity of these compounds is their double character. They are at the same ti

the acid

properties are more prominent than the alcoholic. The hydroxy acids of the benzene series bear the same relations to the benzene hydrocarbons that the hydroxy acids already studied bear to the paraffins. The simplest are those which contain one hydroxyl and one carboxyl, having the formula  $\text{HOC}_6\text{H}_4\text{COOH}$ .

#### MONO-HYDROXYBENZOIC ACIDS, $\text{C}_7\text{H}_6\text{O}_3$

**Salicylic acid**, *ortho*-hydroxybenzoic acid,  $\text{HOC}_6\text{H}_4\text{COOH}(o)$ , in the form of the methyl ester is present in the oil of wintergreen, prepared from the blossoms of *Gaultheria procumbens*. It gets its name from the glucoside salicin, present in the bark and leaves of the willow (*Salix*). It is formed in a number of ways, among which the following should be specially mentioned:

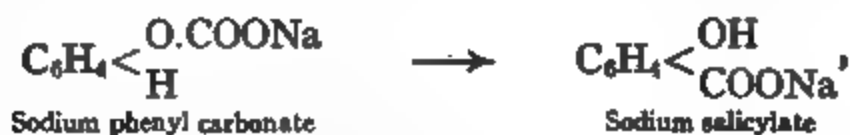
1. By converting *ortho*-aminobenzoic acid into the inner diazonium salt, and boiling with water (408).

NOTE FOR THE STUDENT. — Give the equations representing the reactions.

2. By fusing the potassium salt of *ortho*-sulphobenzoic acid with caustic potash.

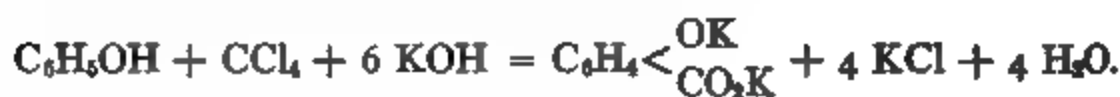
NOTE FOR THE STUDENT. — Write the equation.

3. Salicylic acid is manufactured by heating dry sodium phenolate in an autoclave with carbon dioxide under a pressure of 8 to 10 atmospheres at  $100^\circ$ – $145^\circ$ . At  $100^\circ$  the carbon dioxide is rapidly absorbed, with the formation of sodium phenyl carbonate,  $\text{C}_6\text{H}_5\text{O.CO.ONa}$ , which then undergoes molecular rearrangement into sodium salicylate:—

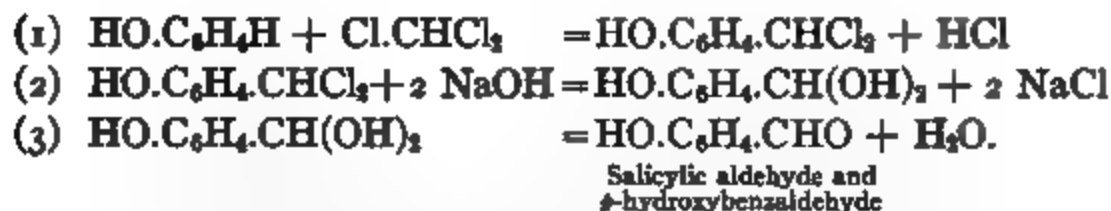


the  $-\text{COONa}$  group entering the benzene ring, and the displaced hydrogen atom taking its place as shown above.

4. By heating phenol with tetra-chloromethane and an alcoholic solution of potassium hydroxide:—

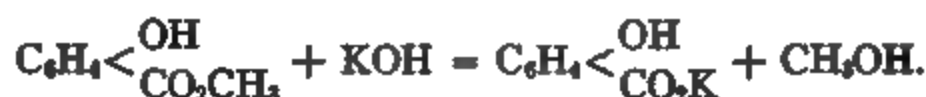


Chloroform acts on phenol in alkaline solution to give salicylic aldehyde and *p*-hydroxybenzaldehyde:—

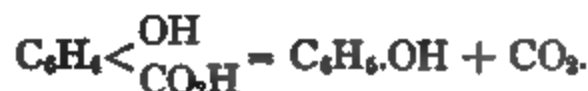


The two aldehydes are separated by distillation in steam, the ortho aldehyde being volatile in steam while the para product is not. This reaction (the Tiemann and Reimer reaction) is used for the purpose of introducing an aldehyde group into phenols. From the aldehydes the acids can be obtained by oxidation.

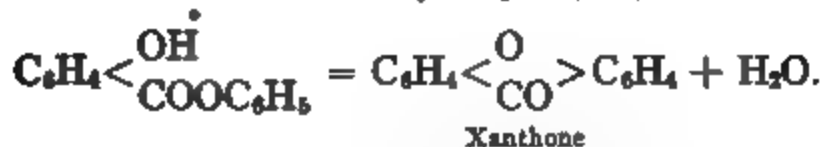
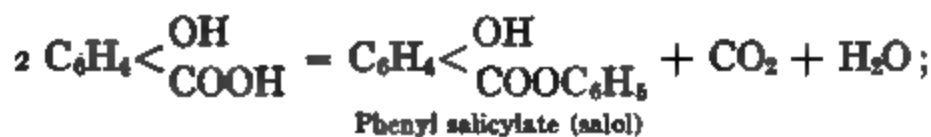
5. By saponifying the methyl salicylate found in oil of wintergreen:—



Salicylic acid crystallizes from hot water in fine needles. It melts at 159°. When heated with sodalime, it breaks down into phenol and carbon dioxide:—



Heated alone it gives phenyl salicylate (salol) and xanthone:—



With ferric chloride, its aqueous solution gives a characteristic, dark violet-blue color, provided no *free* mineral acid is present. Free salicylic acid is antiseptic, preventing putrefaction and fermentation. It is therefore used for preserving foods. It is also used extensively in medicine, especially in rheumatism, and as an antipyretic.



With bromine water, salicylic acid gives a precipitate of tribromophenol bromide,  $C_6H_2Br_3(OBr)_{2,4,6}$ , and this reaction is used for the quantitative determination of salicylic acid:—



When reduced in amyl alcohol solution with metallic sodium salicylic acid is converted into pimelic acid,  $HOOC(CH_2)_4COOH$ .

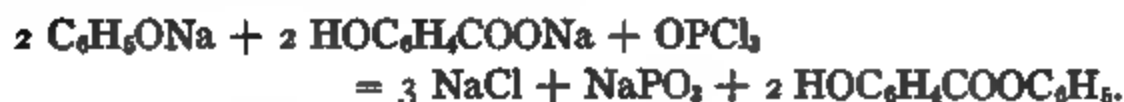
The methyl ester of salicylic acid,  $HO.C_6H_4.CO.OCH_3$ , is the chief constituent of oil of wintergreen. It is made artificially by heating two parts of salicylic acid, two parts of methyl alcohol, and one part of sulphuric acid, and is used in perfumery and in flavoring confectionery, chewing gums, etc. About 900,000 pounds were made in the United States in 1919.

Large quantities of salicylic acid are used in medicine and in the preparation of synthetic remedies (*Aspirin*, *Salol*, etc.) and of the artificial oil of wintergreen. Nearly 3 million pounds of the U. S. P. grade of salicylic acid were made in the United States in 1920. The technical salicylic acid, of which nearly 4 million pounds were made in the United States in 1920, is used in the manufacture of azo dyes (*Alizarin Yellow*, *Chrysamine G*, *Cotton Yellow*, etc.) and in the preparation of aminosalicylic acid,  $H_2N.C_6H_3<\begin{smallmatrix} COOH \\ OH \end{smallmatrix}$ , used in the manufacture of the valuable diamond black.

Salicylic acid forms salts of the general formula  $HOC_6H_4COOM$ ; and, with the alkalis, compounds in which both the phenol hydrogen and the acid hydrogen are replaced by metals, as  $KOC_6H_4COOK$ . The basic calcium salt,  $C_6H_4<\begin{smallmatrix} O \\ CO_2 \end{smallmatrix}>Ca + H_2O$ , is very difficultly soluble in water, and is converted by carbon dioxide into the soluble salt  $(C_6H_4<\begin{smallmatrix} OH \\ CO_2 \end{smallmatrix})_2Ca$ . Salicylic acid forms ethereal salts of the general formula  $HOC_6H_4COOR$ , of which methyl salicylate,  $HOC_6H_4COOCH_3$ , is the best-known example. It forms, also, ether acids of the general formula  $ROC_6H_4CO_2H$ ; and, finally, ether esters of the general formula  $ROC_6H_4CO_2R$ .

**Acetylsalicylic acid** is used in medicine under the name *aspirin*. It is made by heating salicylic acid with acetic anhydride. 1,708,000 pounds were made in the United States in 1920.

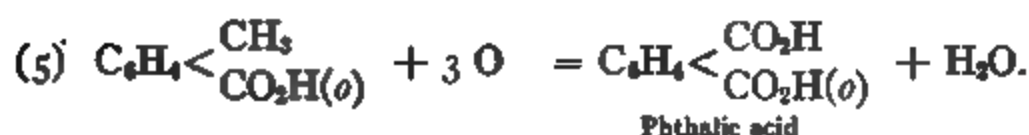
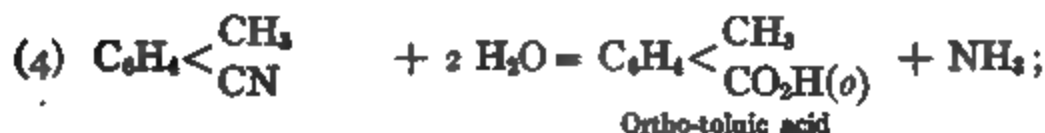
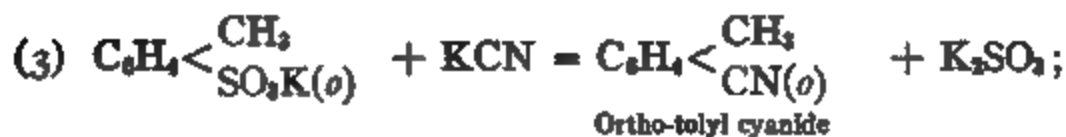
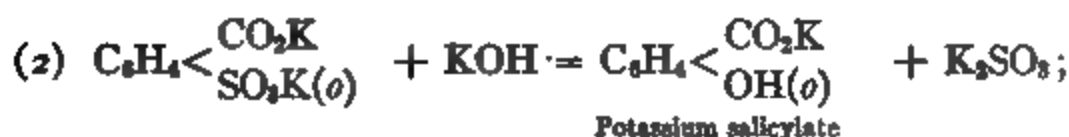
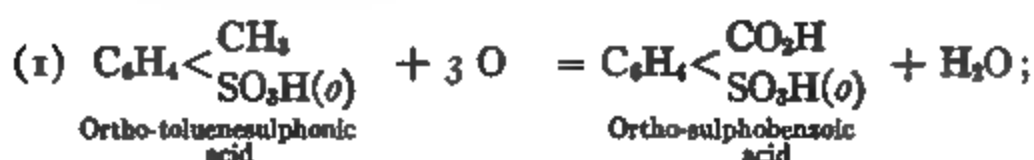
**Phenyl salicylate (salol)**,  $\text{HOC}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$ , is formed when salicylic acid is heated alone to  $200^\circ\text{--}220^\circ$  (421) and when sodium salicylate, sodium phenolate, and phosphorus oxychloride are heated to  $120^\circ\text{--}125^\circ$ :—



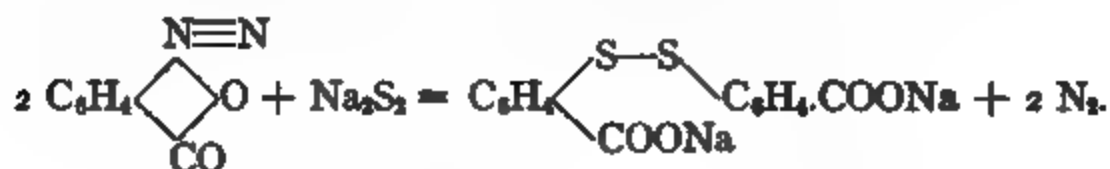
It is a solid that melts at  $43^\circ$ . It is extensively used as an antiseptic, antipyretic, and antirheumatic.

That salicylic acid belongs to the ortho series is clear from the following facts:

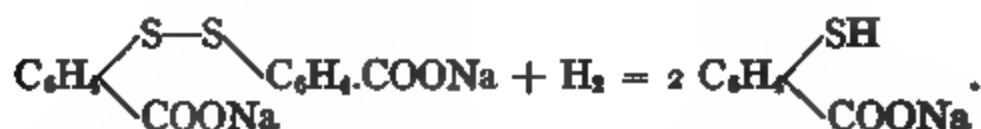
Ortho-toluenesulphonic acid has been converted into ortho-sulphobenzoic acid, and this into salicylic acid. Further, the same toluenesulphonic acid has been converted into ortho-toluic acid, which, by oxidation, yields phthalic acid:—



**Thiosalicylic acid**,  $\text{HS.C}_6\text{H}_4.\text{COOH}(o)$ , is made from anthranilic acid by diazotizing it and decomposing the diazonium carboxylate with sodium disulphide:—



When this dithio acid is reduced it gives thiosalicylic acid:—



Thiosalicylic acid crystallizes in sulphur yellow plates melting at  $163^\circ$ – $164^\circ$  and soluble in hot water. When oxidized it gives *o*-sulphobenzoic acid. It is made on the large scale by the above method and is used in making thioindigo.

**Meta-hydroxybenzoic acid, oxybenzoic acid**,  $\text{HOC}_6\text{H}_4\text{CO}_2\text{H}(m)$ .—This acid is made from meta-aminobenzoic and meta-sulphobenzoic acid by the usual reactions.

It crystallizes from water in needles united to form wart-like masses. It gives no color with ferric chloride. Its connection with meta-phthalic (isophthalic) acid and metaxylene is shown by means of the transformations already referred to (419); that is to say, the same sulphobenzoic acid which, by fusing with caustic potash, yields hydroxybenzoic acid, by fusing with sodium formate yields isophthalic acid. Therefore oxybenzoic acid is a meta compound.

**Para-hydroxybenzoic acid**,  $\text{HOC}_6\text{H}_4\text{COOH}(p) + \text{H}_2\text{O}$ , is formed from the corresponding amino and sulphobenzoic acids; by treating various resins with caustic potash; from anisic acid (425) by heating with hydriodic acid; and by heating potassium phenolate in a current of carbon dioxide to  $220^\circ$ .

NOTE FOR THE STUDENT. — Note the fact that, while *sodium* phenolate, when heated in carbon dioxide, yields salicylic acid, *potassium* phenolate, under the same circumstances, yields para-hydroxybenzoic acid.

The reasons for regarding para-hydroxybenzoic acid as a member of the para series are similar to those which show that oxy-

benzoic acid is a meta compound. The same sulphobenzoic acid that yields para-oxybenzoic acid also yields terephthalic acid.

**Anisic acid**, *p*-methoxybenzoic<sup>1</sup> acid,  $\text{H}_3\text{COC}_6\text{H}_4\text{CO}_2\text{H}(p)$  is formed by the oxidation of anethol,  $\text{H}_3\text{COC}_6\text{H}_4\text{CH:CHCH}_3$ , the chief constituent of the oil of anise seed. It is also made by heating para-hydroxybenzoic acid with caustic potash and methyl iodide and saponifying the methyl ester thus formed. As the formula indicates, it is the methyl ether of para-hydroxybenzoic acid. It is isomeric with methyl salicylate. By boiling with a solution of caustic alkali the latter is saponified, while anisic acid is not. When anisic acid is distilled with lime, anisol is formed.

### DIHYDROXYBENZOIC ACIDS, $\text{C}_7\text{H}_6\text{O}_4$

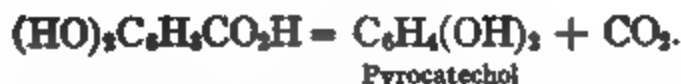
**Protocatechuic acid**, 3,4-dihydroxybenzoic acid,  
 $(\text{HO})_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$ ,

is a frequent product of the fusion of resins with alkali. The following substances, among others, yield it: oil of cloves, piperic acid, catechin, gum benzoin, asafoetida, vanillin, etc. It is made from sulpho-*m*-hydroxybenzoic acid, and from sulpho-*p*-hydroxybenzoic acids by fusing with caustic potash.

**NOTE FOR THE STUDENT.** — What analogy is there between the fact that protocatechuic acid is formed from sulpho-*m*-hydroxybenzoic acid and from sulpho-*p*-hydroxybenzoic acid, and the fact that pseudocumene is formed from bromometaxylene and from bromoparaxylene? What conclusion may be drawn regarding the relations of the two hydroxyl groups, and the carboxyl in protocatechuic acid?

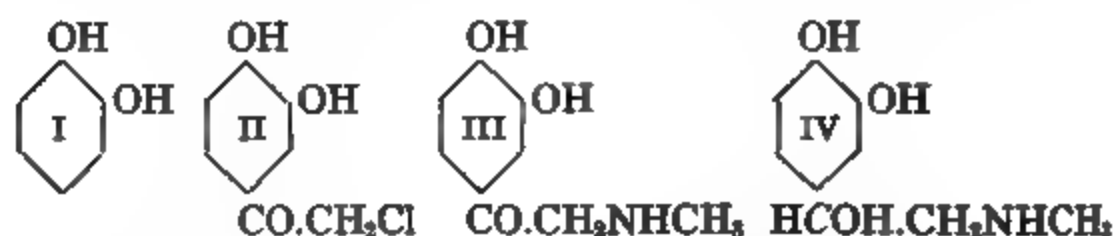
It is made synthetically together with 2,3-dihydroxybenzoic acid by heating pyrocatechol with a solution of ammonium carbonate.

By distillation with lime, protocatechuic acid breaks down into pyrocatechol and carbon dioxide: —



<sup>1</sup> *Methoxy* is derived from *methoxyl*, the name given to the ether group,  $\text{OCH}_3$ . In a similar way  $\text{OC}_2\text{H}_5$  is called *ethoxyl*;  $\text{OC}_6\text{H}_5$ , *phenoxyl*, etc.

**Adrenaline, suprarenine,  $C_9H_{13}O_3N$** , is found in the medulla of the suprarenal capsules of all vertebrates and is characterized by its remarkable effect on the blood pressure. As small an amount as 0.000002 gram injected intravenously produces a noticeable effect on the blood pressure. It is usually made from the suprarenal glands of the sheep or other animals by extracting them with dilute acid and precipitating the base with ammonia. It is an unstable, weak base which decomposes rapidly when in aqueous solution, but is fairly stable in the solid state or in the form of the hydrochloride, in which form it is generally sold. It is distinguished readily by the green color it gives with a solution of ferric chloride. (Compare with pyrocatechol.) It yields protocatechuic acid on oxidation and, when distilled with sodalime, methylamine. When benzoylated with benzoyl chloride it forms a tribenzoate. It is made synthetically from pyrocatechol: (I) This is first condensed with monochloroacetic acid in the presence of phosphorus oxychloride to chloroacetyl pyrocatechol (II) which gives the methylamino compound of the ketone (III) when treated with methylamine. By means of sodium amalgam the ketone is then reduced to *dl*-adrenaline (IV): —

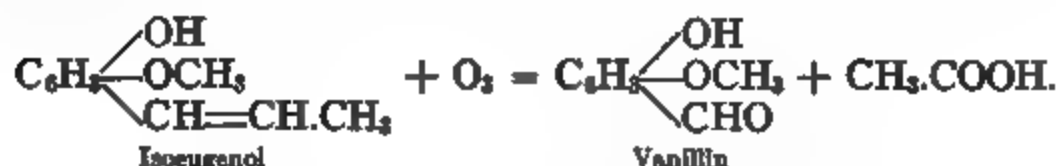


The synthetic product is optically inactive; the natural product is levorotatory and is much more active physiologically than the dextroproduct or the optically inactive base. By means of the salt with *d*-tartaric acid, the levorotatory adrenaline is separated from the synthetic product and is used in medicine and in surgery.

**Vanillin**, the monomethyl ether of protocatechuic aldehyde,



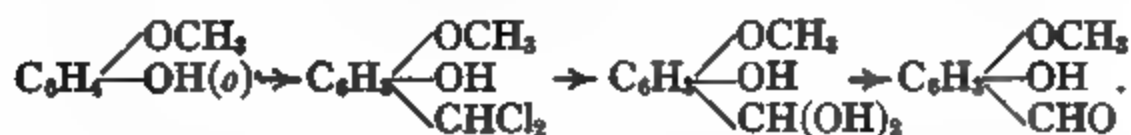
is very widely distributed in the plant world, usually,\* however, in small quantity. It is the characteristic constituent of the vanilla bean, which contains about 2 per cent. It is made on the large scale by oxidizing isoeugenol with ozone or other oxidizing agents:—



The isoeugenol is made from eugenol, the chief constituent of the oil of cloves, by heating it with a solution of caustic soda, which causes the shifting of the double bond in the side chain. (See allyl cyanide and crotonic acid.)



It has been made synthetically from guaiacol by treating it with chloroform and a solution of an alkali. (Analogous to the preparation of salicylic aldehyde.)

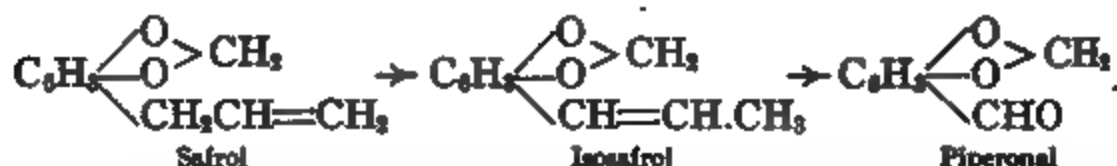


It crystallizes in colorless needles melting at 80°–81°, which are somewhat soluble in water. The aqueous solution gives a blue color with ferric chloride. It gives an oxime melting at 121°–122° and an acetyl compound melting at 71°, and these compounds are used to identify vanillin. Large quantities of vanillin are used in the manufacture of chocolate, ice cream, confectionery, and vanilla extract. It is also used in the manufacture of perfumes.

Piperonal, heliotropin, the methylene ether of protocatechuic

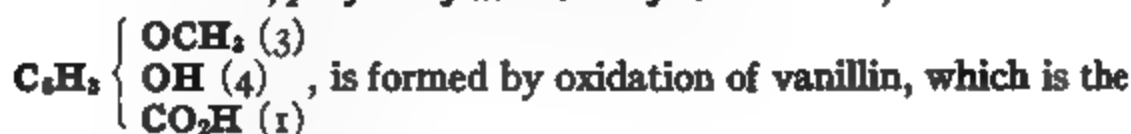
aldehyde,  $\text{C}_6\text{H}_5-\begin{array}{c} \text{CHO} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array} > \text{CH}_2$ , is made on the large scale by oxidiz-

ing isosafrol, which is obtained from safrol by molecular rearrangement with solutions of the alkalis:—



Safrol is the chief constituent of the oil of sassafras and of camphor oil. Heliotropin has also been made by treating an alkaline solution of protocatechuic aldehyde with methylene iodide. It forms colorless crystals, having the odor of heliotrope, which melt at  $35^\circ$ – $36^\circ$ . It is made on the large scale from safrol and is used in the manufacture of perfumes.

Vanillic acid, *p*-hydroxy-*m*-methoxybenzoic acid,



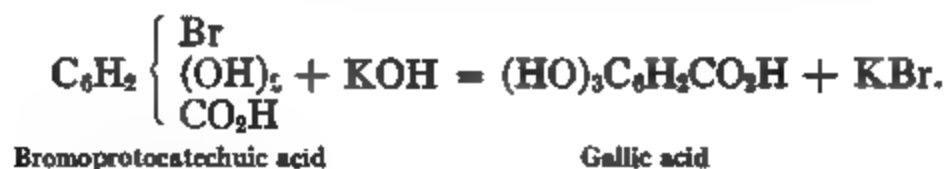
corresponding aldehyde. It is the mono methyl ether of protocatechuic acid, and gives guaiacol when distilled with lime.

#### TRIHIDROXYBENZOIC ACIDS, $\text{C}_7\text{H}_4\text{O}_5$

Gallic acid, 3,4,5-trihydroxybenzoic acid,



— Gallic acid occurs in nutgalls, sumach, Chinese tea, and in many other plants. It is formed by boiling tannin or tannic acid with dilute sulphuric acid and by fusing bromoprotocatechuic acid or bromo-3,5-dihydroxybenzoic acid with caustic potash:—



Gallic acid is also obtained together with its isomer, pyrogallolcarboxylic acid, by heating a solution of pyrogallol with potassium bicarbonate.

NOTE FOR THE STUDENT. — Deduce the structure of gallic acid from these methods of synthesis of the acid. See note on page 390. What is the structure of pyrogallolcarboxylic acid?

Gallic acid is prepared on the large scale from the mother liquors obtained in extracting tannin from nutgalls (see below). These are inoculated with certain microorganisms (*penicillium glaucum*, *aspergillus niger*, etc.) which hydrolyze the tannin to glucose and gallic acid. After the fermentation has ceased, the gallic acid is filtered off and purified by recrystallization from water.

Gallic acid is difficultly soluble in cold water, easily in hot water, alcohol, and ether. Its solution gives, with a little ferric chloride solution, a blue-black precipitate, which dissolves in excess of ferric chloride, forming a dark green solution (iron ink). It is readily oxidized, reduces Fehling's solution and salts of the noble metals, and its alkaline solution absorbs oxygen. It is not precipitated by gelatin solution (distinction from tannin). When distilled, it yields pyrogallol (pyrogallic acid) and carbon dioxide:—



Gallic acid is used in making pyrogallol, in the manufacture of anthraquinone dyes, medicinal remedies, and writing inks.

Tannins, tannic acids, are widely distributed in the plant world and are largely used for the purpose of converting hides into leather<sup>1</sup> (tanning). The name is applied to a group of substances which act as weak acids, have an astringent taste, give a blue-black or green color with ferric salts, and precipitates with solutions of gelatin, proteins and the alkaloids. They are closely related to the hydroxy aromatic acids and give one or more of these acids on hydrolysis. The tannin of Chinese nutgalls, when hydrolyzed with dilute sulphuric acid, gives gallic acid and glucose in the proportion of ten molecules of the acid to one of glucose, and is closely related to, or identical with, a *penta-digalloylglucose* made synthetically by Emil Fischer from gallic acid and glucose:—



This substance, which contains five residues of digallic acid,



<sup>1</sup> See *Industrial Chemistry*, edited by Allen Rogers, 3d ed; p. 1092.



in place of the five hydroxyl hydrogen atoms of glucose, bears a remarkable resemblance to the tannin obtained from Chinese nutgalls and gives all the reactions characteristic of that substance. Like the natural tannin it is optically active and gives the same amount of glucose and gallic acid when hydrolyzed with dilute sulphuric acid.

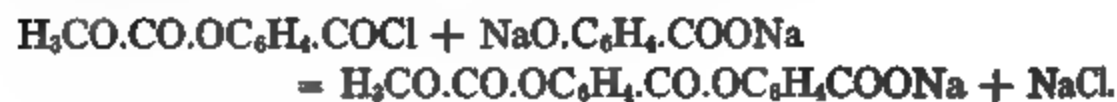
The commercial gallotannin, obtained by evaporating aqueous extracts of nutgalls, is a white, or yellowish, amorphous powder, readily soluble in water and alcohol, but insoluble in ether, chloroform, and benzene. It is a typical colloid and is precipitated from its aqueous solutions by hydrochloric and sulphuric acids and by sodium and potassium chlorides. Animal skin removes it completely from its aqueous solutions, and it gives precipitates with solutions of gelatin, egg albumen, and the alkaloids. It decomposes carbonates and is a weak acid. With solutions of ferric salts it gives a bluish-black coloration or a precipitate according to the concentration.

It is used in medicine, as a mordant in dyeing, and in the manufacture of writing inks. It is not used as a tanning agent.

**Depsid.** — The digallic acid, mentioned above as a constituent of Fischer's artificial tannin, is an example of a class of compounds called *depsides* (Gr. *depsein*, to tan). The simplest of these is derived from *p*-hydroxybenzoic acid,  $\text{HO.C}_6\text{H}_4.\text{COOH}(p)$ . The acid is first treated in aqueous, alkaline solution with methyl chlorocarbonate to obtain the carbomethoxy compound:—



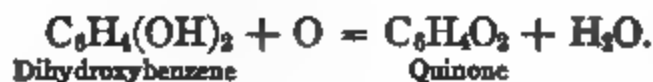
The phenol group in the acid is thus protected or rendered inactive. The carbomethoxy compound is then treated with phosphorus pentachloride and the chloride formed is combined with another molecule of *p*-hydroxybenzoic acid in aqueous, alkaline solution:—



When this product is saponified by cold, dilute alkali it gives methyl alcohol, carbon dioxide, and the sodium salt of the *depside* of *p*-hydroxybenzoic acid,  $\text{HO.C}_6\text{H}_4.\text{CO.OC}_6\text{H}_4.\text{COOH}$ , in which the *p*-hydroxybenzoyl group replaces the hydrogen of the phenol hydroxyl group. As this substance contains *two* residues of *p*-hydroxybenzoic acid, it is called a di-depside, while those containing three and four residues are known as tri- and tetra-depsides. The di-depsides of gallic acid and of protocatechuic acid give precipitates with dilute solutions of gelatin analogous to those obtained with tannin. All the depsides are hydrolyzed by heating with solutions of the alkalies and yield salts of the hydroxy aromatic acids.

### QUINONES

The quinones are compounds formed by the oxidation of the *o*- and *p*- dihydroxy derivatives of the aromatic hydrocarbons:—



The simplest one, and the best-known, is called quinone or *p*-benzoquinone, from the fact that it was first obtained by the oxidation of quinic acid, hexahydrotetrahydroxybenzoic acid,  $\text{C}_6\text{H}_7(\text{OH})_4\text{COOH}$ .

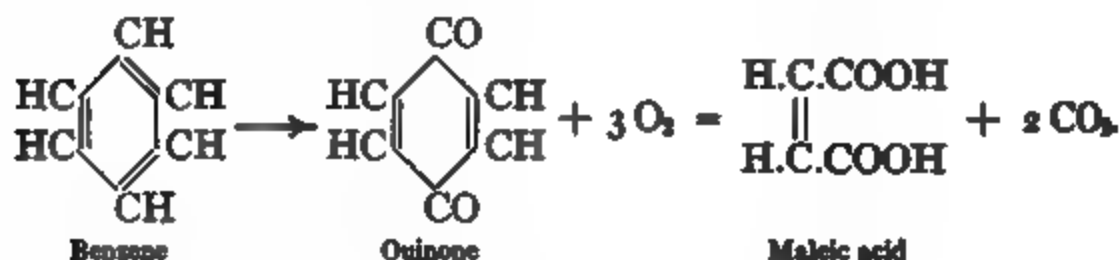
*p*-Benzoquinone,  $\text{C}_6\text{H}_4\text{O}_2$ , results from the oxidation of para-derivatives of benzene, such as *p*-phenylenediamine, *p*-aminophenol, sulphanilic acid, and *p*-phenolsulphonic acid. It is usually made by the oxidation of aniline by means of chromic acid mixture (387). As hydroquinol is now a commercial product, quinone is most conveniently made from it by oxidation.

It crystallizes in yellow, monoclinic prisms, which melt at  $115.7^\circ$ , and have a penetrating, characteristic odor resembling that of chlorine. It turns brown when exposed to the light, and the aqueous solution colors the skin brown. It sublimes in golden, yellow needles and is volatile with steam, though with slight decomposition. When heated with acetic anhydride in the presence of sulphuric acid quinone gives the tri-acetate of hydroxyhydroquinol:—

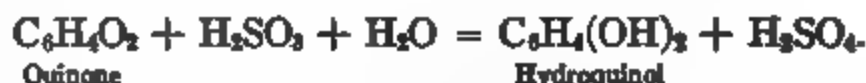


With hydroquinol, quinone forms an addition product,  $C_6H_4O_2 + C_6H_4(OH)_2$ , known as *quinhydrone*. It crystallizes in green prisms having a metallic luster and is also formed as an intermediate product in the oxidation of hydroquinol or in the reduction of quinone.

When benzene is oxidized by passing air saturated with benzene vapor over heated vanadium oxide it gives quinone and maleic acid:—



Reducing agents (hydriodic acid, sulphurous acid, hydroxylamine, etc.) convert it into hydroquinol:—



When reduced with hydrogen in the presence of finely divided nickel heated to the proper temperature, quinone first gives hydroquinol, which then takes up six atoms of hydrogen to form cyclohexa-1,4-diol (quinitol) I:—



This substance conducts itself like a saturated, secondary alcohol, *e. g.*, it gives a diketone, cyclohexa-1,4-dione II, on oxidation, and it has also been made by the reduction of this diketone.

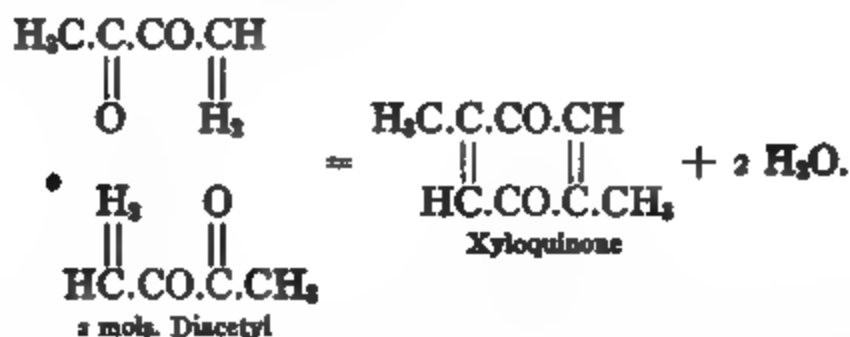
Quinone is an unsaturated compound, and in solution in chloroform combines with two and four atoms of bromine to form a di- and a tetra-bromide,  $C_6H_4O_2Br_2$  and  $C_6H_4O_2Br_4$ .

The fact that quinone can only be obtained from *para* compounds by oxidation and that it yields hydroquinol (*p*-dihydroxy-

benzene) on reduction leads to the conclusion that the oxygen atoms are in the *para* position to each other, as shown in the structural formula given above.

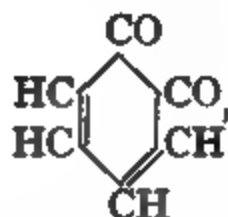
According to this view of the structure of quinone it is a *para*-diketodihydrobenzene, and is a derivative of cyclohexa-1,4-diene (329), in which four *para* hydrogen atoms are replaced by two oxygen atoms. Like cyclohexa-1,4-diene it is unsaturated and takes up two and four atoms of bromine, and like the diketones it forms a monoxime,  $C_6H_4O(NO\dot{H})$ , and a dioxime,  $C_6H_4(NO\dot{H})_2$ , with hydroxylamine hydrochloride. The monoxime is identical with *p*-nitrosophenol (376) obtained by the action of nitrous acid on phenol.

Homologues of *p*-benzoquinone are also known, such as toluquinone,  $C_8H_8O_2CH_3$ , and xyloquinone,  $C_8H_8O_2(CH_3)_2$ . The latter compound is made synthetically by the action of solutions of the alkalis on diacetyl:—



They are all colored compounds which are reduced to colorless dihydroxy derivatives of the aromatic hydrocarbons by nascent hydrogen.

*o*-Benzoquinone,



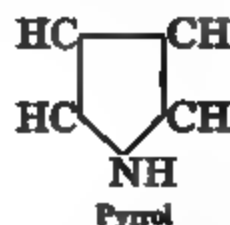
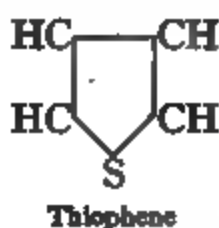
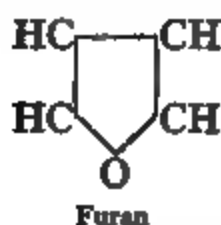
isomeric with *p*-benzoquinone, has been obtained by oxidizing pyrocatechol in ethereal solution with silver oxide. It crystallizes in red plates, is unstable and decomposes when heated to  $60^\circ$ - $70^\circ$ . It differs from *p*-benzoquinone in being non-volatile with steam and having no odor. It is reduced to pyrocatechol

by sulphurous acid. It is the diketone derivative of cyclohexa-1,3-diene (329).

Quinones in which the oxygen atoms are in the meta position to each other are unknown.

### FURAN, THIOPHENE, PYRROL

These three substances have been shown to be related structurally to benzene as indicated in the formulas below : —



Furan is regarded as benzene in which an oxygen atom has been substituted for the group  $\text{—HC=CH—}$ . Similarly, thiophene is derived from benzene by the substitution of a sulphur atom, and pyrrol, by the substitution of an imino group,  $\text{NH}$ , for two of the  $\text{=CH—}$  groups.

Derivatives of all three compounds are formed from mucic acid (206)  $\text{HO}_2\text{C}(\text{CHOH})_4\text{CO}_2\text{H}$ . When distilled this gives *pyromucic acid*, which is a carboxyl derivative of furan; when the ammonium salt of mucic acid is distilled, pyrrol is obtained; and, when mucic acid is distilled with barium sulphide, a carboxyl derivative of thiophene is obtained. *Fural*, *furfural*,  $\text{C}_4\text{H}_3\text{O}.\text{CHO}$ , is obtained from pentoses by distilling them with hydrochloric acid. The yield is quantitative, and this fact is taken advantage of for the purpose of determining the amounts of pentoses present in various substances (218). Large quantities of fural may be made from corn cobs. It is a liquid boiling at  $162^\circ$ .

Thiophene,  $\text{C}_4\text{H}_4\text{S}$ , occurs in coal tar benzene and resembles benzene very closely. It can be made synthetically in a number of ways.

Pyrrol,  $\text{C}_4\text{H}_4\text{NH}$ , is contained in coal tar in small quantity; in larger quantity in *Dippel's oil*, formed when bones are dis-

tilled. Many substances occurring in nature are related more or less closely to pyrrol.

### PYRIDINE BASES, $C_nH_{2n-1}N$

Pyridine was first isolated from *bone oil*, a product resulting from the heating of bones in closed retorts for the purpose of making bone black or ivory black. Besides pyridine, bone oil contains higher homologues, most of which are methyl derivatives of pyridine. These pyridine bases are also found in the distillation products of wood, coal, lignite, and bituminous shales. At present they are obtained from coal tar, although this substance contains only 0.05 to 0.1 per cent of these bases.<sup>1</sup> They form an homologous series analogous to the hydrocarbons of the benzene series:—

Pyridine	. . . . .	$C_5H_5N$
Picolines	. . . . .	$C_6H_7N$
Lutidines	. . . . .	$C_7H_9N$
Collidines	. . . . .	$C_8H_{11}N$
Parvolines	. . . . .	$C_9H_{13}N$
etc.		etc.

Soon after the discovery of the pyridine bases in bone oil they were found among the products formed when cinchonine, an alkaloid present together with quinine in cinchona bark, is distilled with caustic alkalis. At the present time it is known that a large number of the plant alkaloids, some of which are valuable medicinal remedies, are derivatives of these bases. The formation of pyridine bases when bones are heated is due to the presence of fats and proteins in the bones, for when the fats are removed, no pyridine bases are formed. The fats give acrolein on heating and the proteins (gelatin, etc.) form ammonia, methylamine, etc. These substances react with one another at the high temperature to form the pyridine bases. Homo-

<sup>1</sup> See *Coal Tar and Ammonia*, by G. Lunge, 5th ed. 1916, Part II, Coal Tar, p. 895.

logues of pyridine are formed whenever the compounds of the aldehydes of the fatty series with ammonia (aldehyde ammonias) are heated either alone or with aldehydes. Thus, acetic aldehyde ammonia gives as the chief product, 2-methyl-5-ethylpyridine:—



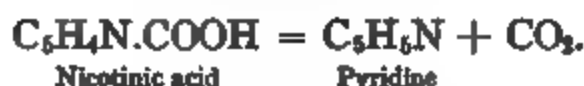
While acrolein ammonia gives  $\beta$ -picoline:—



$\beta$ -Picoline is also formed by the distillation of strychnine and brucine with lime.

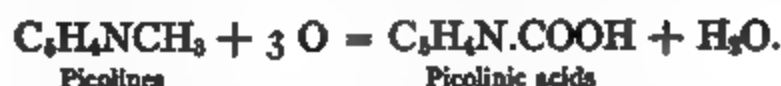
Pyridine and its homologues are formed in considerable quantity by distilling glycerol with ammonium phosphate.

Pyridine,  $\text{C}_5\text{H}_5\text{N}$ , is a colorless liquid, with a characteristic penetrating odor. It boils at  $115.1^\circ$ . It has been obtained pure by fractional distillation of bone oil and of the bases from coal tar, but is best made by distillation of its carboxylic acid with lime:—



This acid, which bears the same relation to pyridine that benzoic acid bears to benzene, is obtained by the oxidation of the alkaloid nicotine, found in tobacco. Pyridine is present in crude ammonia. It is miscible with water in all proportions and the mixture having the composition  $\text{C}_5\text{H}_5\text{N} + 3 \text{ H}_2\text{O}$  has the boiling point  $92^\circ\text{--}93^\circ$ . Pyridine is a weak, monacid base, forming salts like  $\text{C}_5\text{H}_5\text{N.HCl}$ ,  $\text{C}_5\text{H}_5\text{N.HNO}_3$ ,  $\text{C}_5\text{H}_5\text{N.H}_2\text{SO}_4$ , etc. The ferrocyanide is only sparingly soluble in cold water and is used to separate it from its homologues and to identify it. It does not turn litmus blue. Commercial pyridine is used in denaturing alcohol and in synthetical work. It is also used in making piperidine on the large scale. It is a tertiary amine, since it does not give an acetyl derivative with acetyl chloride and combines with methyl iodide to form methyl pyridonium

iodide,  $C_5H_5N < \underset{I}{CH_3}$ . A solution of this iodide in water gives methylpyridonium hydroxide,  $C_5H_5N < \underset{OH}{CH_3}$ , when treated with silver oxide, and this hydroxide is a strong base. Pyridine is a remarkably stable substance, even more stable than benzene. It may be boiled with nitric or chromic acids without undergoing any change, and this fact is made use of in purifying it. The homologues of pyridine are oxidized to pyridinecarboxylic, or picolinic, acids, just as the homologues of benzene give the carboxylic acids of benzene on oxidation:—



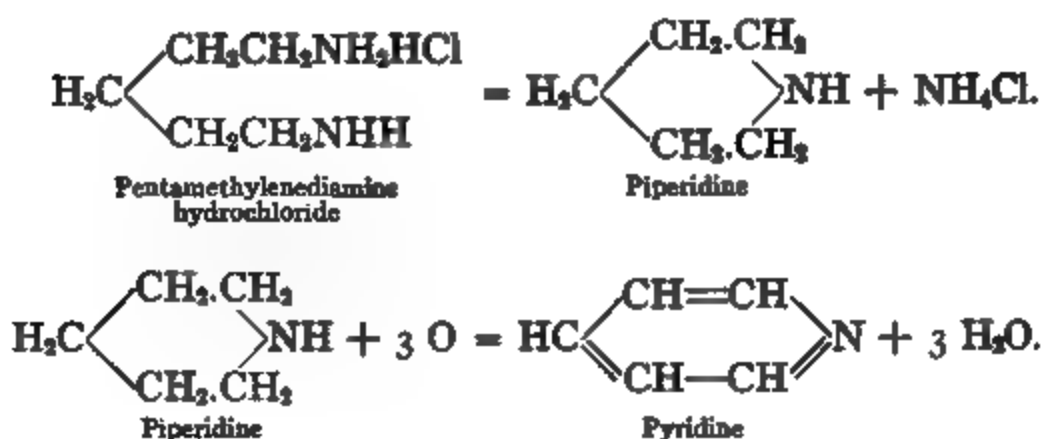
In its conduct towards reagents it acts remarkably like benzene, but it does not form substitution products as readily as benzene does. Thus it forms a sulphonic acid only when heated to a very high temperature with sulphuric acid, and a nitro compound only when heated to  $300^\circ$  with mixed acid (308). The sodium salt of the sulphonic acid gives a hydroxypyridine when fused with caustic soda, and this compound acts like a phenol. Nitropyridine on reduction is converted into aminopyridine, which resembles aniline closely. It can be diazotized like aniline and the diazonium salt combines with phenols and amines to form azo compounds. With chlorine and bromine pyridine forms halogen substitution products.

Pyridine has been made synthetically from trimethylene bromide (304) by first converting this into the cyanide and the cyanide into pentamethylenediamine by reduction with sodium in alcoholic solution:—

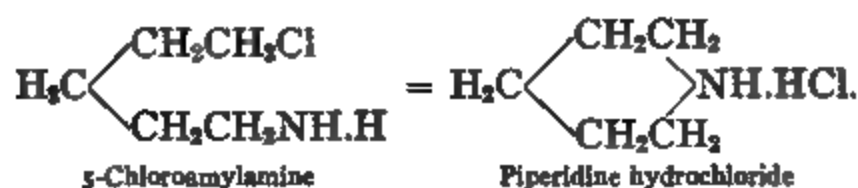


When the hydrochloride of this base is distilled it gives piperidine (hexahydropyridine) and this, when oxidized by heating it with concentrated sulphuric acid to  $300^\circ$ , gives pyridine:—

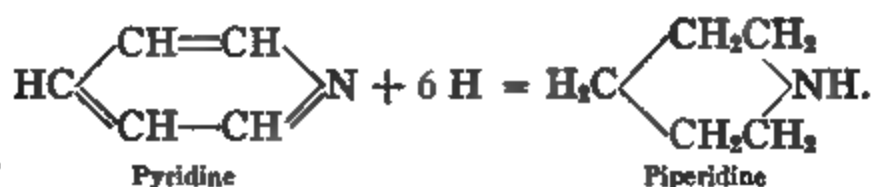




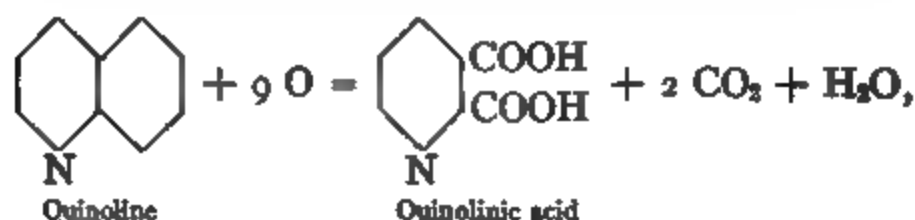
Piperidine hydrochloride also results when an aqueous solution of 5-chloroamylamine is heated on the water bath:—



When the boiling alcoholic solution of pyridine is treated with sodium, piperidine is formed:—

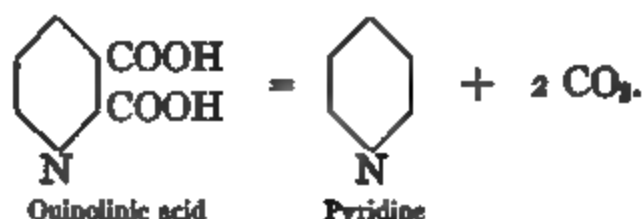


It will be seen from the above reactions that the relation between pyridine and piperidine is the same as that between benzene and cyclohexane. Another method of formation of pyridine, which throws light on its structure, is from quinoline, a base which is also present in coal tar and whose structure is known (507). Quinoline when oxidized gives quinolinic acid (pyridine-dicarboxylic acid):—

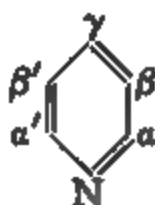


analogous to the formation of phthalic acid by the oxidation of

naphthalene. Quinolinic acid when distilled with lime gives pyridine, just as phthalic acid gives benzene :



According to these methods of formation and the reactions of pyridine it is benzene in which a nitrogen atom takes the place of one CH group.

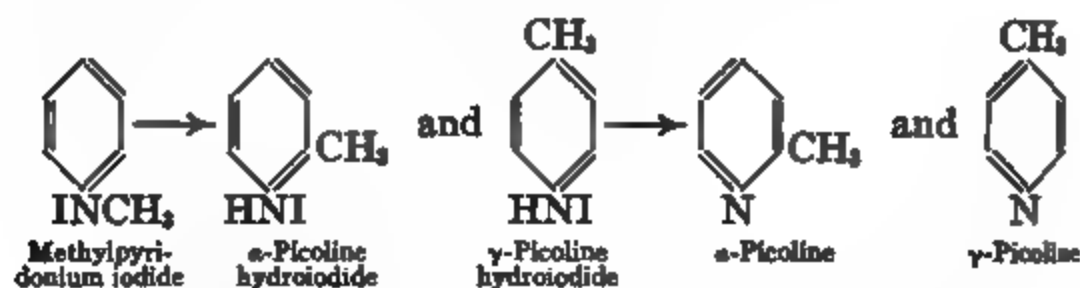


This formula is in accord with the remarkable stability of the substance and with the fact that it is a tertiary amine, but gives a hexahydro addition product, piperidine, on reduction, which is a secondary amine. According to this formula of pyridine it is in a sense a monosubstitution product of benzene and should yield three monosubstitution products corresponding to the ortho-, meta-, and para- disubstitution products of benzene. For example, there should be three methylpyridines or picolines, three pyridinecarboxylic acids, etc. The three picolines, all of which are present in coal tar and in bone oil, are represented by the following formulas : —



They are designated  $\alpha$ -,  $\beta$ -, and  $\gamma$ -picoline or 2-, 3-, and 4-picoline according to the position of the methyl group.  $\alpha$ - and  $\gamma$ -Picoline but not the  $\beta$ -product are formed when methylpyridonium iodide

is heated in a sealed tube to about  $300^{\circ}$  and the hydroiodides formed are distilled with a solution of an alkali:—



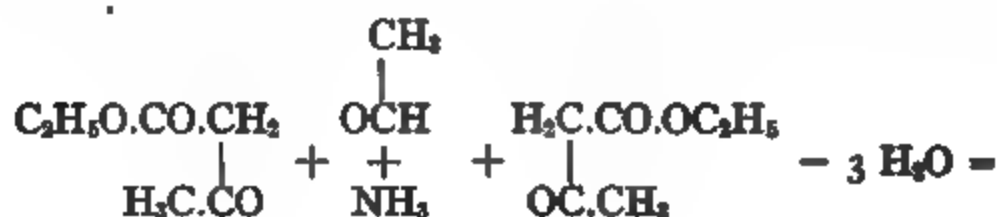
When oxidized  $\alpha$ -picoline gives picolinic acid, while  $\beta$ -picoline yields nicotinic acid (first obtained by the oxidation of nicotine, whence the name) and  $\gamma$ -picoline gives isonicotinic acid. When distilled with lime all these acids give pyridine.

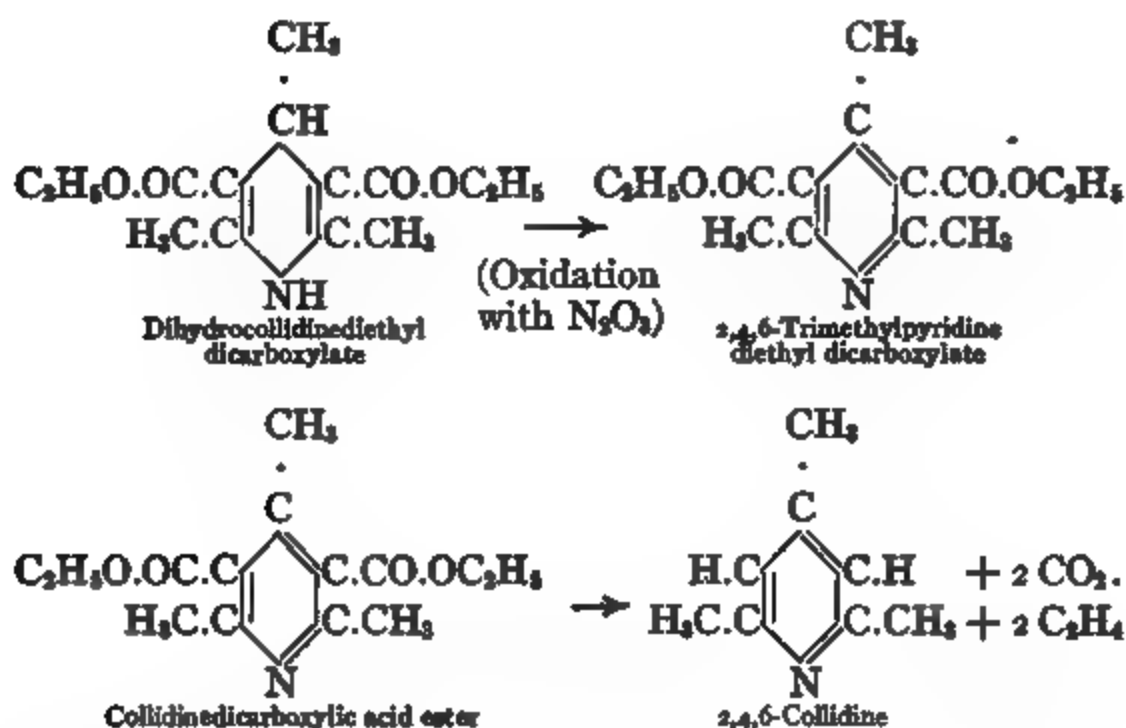
**Lutidines**,  $\text{C}_8\text{H}_9(\text{CH}_3)_2\text{N}$ . — The six dimethylpyridines (2, 3; 2, 4; 2, 5; 2, 6; 3, 4; and 3, 5) predicted by the theory are all known and are present in coal tar. When oxidized they are first converted into monobasic acids,  $\text{C}_8\text{H}_7\text{N}(\text{CH}_3)_2\text{COOH}$  and then into dibasic acids,  $\text{C}_8\text{H}_5\text{N}(\text{COOH})_2$ . The monobasic acids give the three picolines when distilled with lime, while the dibasic acids yield pyridine.

**$\beta$ -Ethylpyridine**,  $\text{C}_8\text{H}_9\text{NC}_2\text{H}_5$ , isomeric with the lutidines, is formed in the distillation of cinchonine with potash, or of brucine with lime. It gives nicotinic acid on oxidation.

**Conyrrine**, 2-propylpyridine,  $\text{C}_9\text{H}_{11}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{N}$ , is obtained from its hexahydrate, conine (442), by distillation of its hydrochloride with zinc dust. It boils at  $166^{\circ}$ – $168^{\circ}$ . It is converted into picolinic acid by oxidation and into inactive conine on reduction with hydriodic acid.

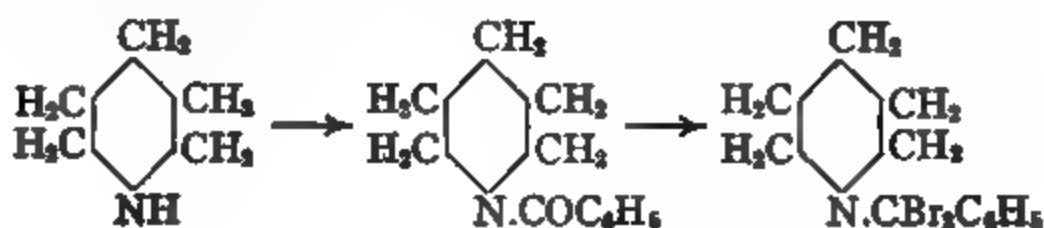
**Collidine**, 2,4,6-trimethyl-pyridine,  $\text{C}_8\text{H}_9(\text{CH}_3)_3\text{N}$ , isomeric with conyrrine, is obtained from collidinedicarboxylic acid ester by distillation with sodalime. The ester is made from acetoacetic ester, acetic aldehyde and ammonia:—

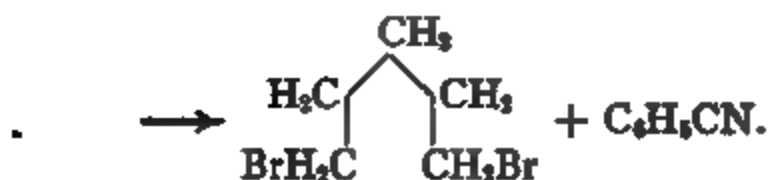




It boils at  $171^\circ$ – $172^\circ$  and is fairly soluble in cold water, but only slightly soluble in hot water.

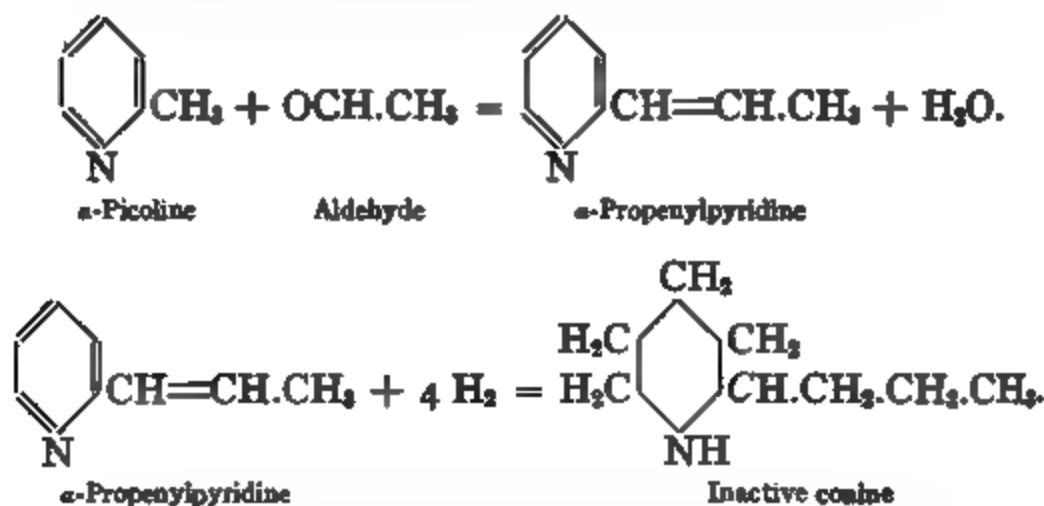
Piperidine, hexahydropyridine,  $\text{C}_5\text{H}_{11}\text{N}$ , was first obtained from piperine, the alkaloid of pepper. Piperine is piperyl-piperidine, and when hydrolyzed it gives piperidine and piperic acid. Piperidine is now made on the large scale from pyridine by reducing it in a boiling solution in ethyl alcohol with sodium. It is a colorless liquid having a strong ammoniacal odor and also the odor of pepper. It is miscible with water in all proportions. It has a very caustic taste and is a very much stronger base than pyridine, turning litmus blue. It solidifies at  $-13^\circ$ , boils at  $106.2^\circ$  and is very poisonous. It is a secondary amine, as it gives an acetyl compound with acetyl chloride and a nitroso compound with nitrous acid. When the benzoyl derivative of piperidine is treated with phosphorus pentabromide it gives a dibromo product which when distilled decomposes into pentamethylene dibromide and phenyl cyanide:—





This is the best method of making pentamethylene dibromide.

Conine, 2-propylpiperidine,  $\text{H}_2\text{C} \begin{array}{l} \text{CH}_2.\text{CH}_2 \\ >\text{NH} \\ \text{CH}_2.\text{CH}.\text{C}_2\text{H}_5 \end{array}$ , occurs with other bases in spotted hemlock (*conium maculatum*). It is a colorless liquid, having a stupefying odor and boiling at  $167^\circ$ . It is but slightly soluble in water and is extremely poisonous. Both the dextro- and levorotatory forms occur in nature. (Does it contain an asymmetric carbon atom?) The *d*-form is the one used in medicine. It was the first alkaloid to be made synthetically. The steps taken are as follows:—



The synthesis of pyridine from trimethylene bromide (437) and of  $\alpha$ -picoline from pyridine (439) have already been given. The inactive conine can be resolved into the two active forms by means of the salts formed with *d*-tartaric acid.

### TERPENES AND CAMPHORS

Most of the hydrocarbons occurring in the volatile oils,<sup>1</sup> obtained from plants or parts of plants (leaves, roots, flowers, fruits, rinds) by distillation with steam, have the composition

<sup>1</sup> See *Volatile Oils*, by E. Gildemeister, 2d ed. Translated by E. Kremers, 1913.

and molecular weight represented by the formula,  $C_{10}H_{16}$ . The best known representative of this class of hydrocarbons is pinene, the chief constituent of the oil of turpentine (see footnote, 418). For this reason they were called *Terpenes*. At the present time terpenes are known having the formula,  $C_5H_8$ , such as isoprene found among the products of the dry distillation of rubber, and these are designated *Hemiterpenes*. More complicated terpenes having the formula,  $C_{15}H_{24}$ , and hence called *Sesquiterpenes*, are also constituents of many volatile oils. Finally there are terpenes,  $(C_5H_8)_x$ , such as rubber and gutta percha, whose molecular weights are unknown, and these are called *Polyterpenes*. All of these terpenes are unsaturated compounds. Some contain one double bond and unite with one molecule of hydrochloric acid or two atoms of bromine, others contain two double bonds and combine with two molecules of hydrochloric acid or four atoms of bromine. Several of them combine with water to form hydrates. The hemiterpenes and terpenes are readily polymerized by heat or the action of sulphuric acid, and several of the polyterpenes are depolymerized by the action of heat. Many of the terpenes are closely related to the hydrogen addition products of *p*-cymene and can be converted into *p*-cymene by mild oxidation, while more energetic oxidation gives *p*-toluic and terephthalic acids. A few contain the *m*-cymene nucleus, sylvestrene for example.

## HEMITERPENES

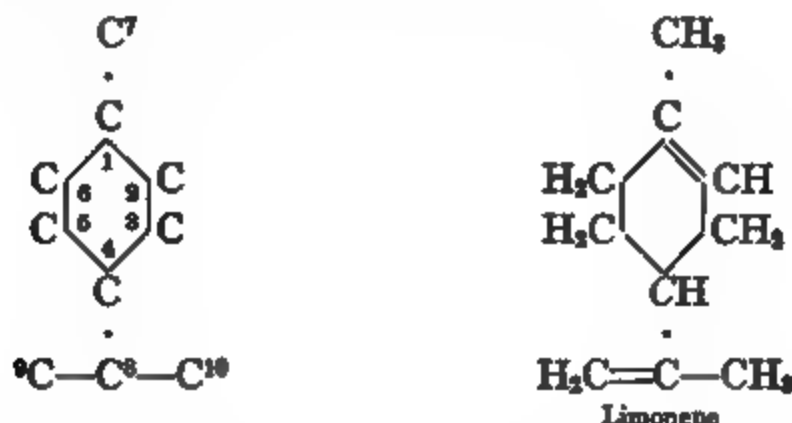
**Isoprene, 2-methyl-1,3-butadiene,  $C_5H_8$** , is the best-known representative of this class. It is formed in small quantity as one of the products of the distillation of natural rubber and by the decomposition of turpentine or dipentene at a dull red heat. It is a colorless liquid, boiling at  $37^\circ$ . It has been shown to be

$\beta$ -methyldivinyl or 2-methyl-1,3-butadiene, 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{C}:\text{C}-\text{CH}:\text{CH}_2 \end{array}$$

as it gives a dibromide,  $\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{H}_3\text{C} \end{array} > \text{CBr}.\text{CH}_2.\text{CH}_2.\text{Br}$ , when treated with hydrobromic acid, identical with that obtained from



gen addition products. The carbon atoms in the formula of *p*-cymene are numbered as follows: —

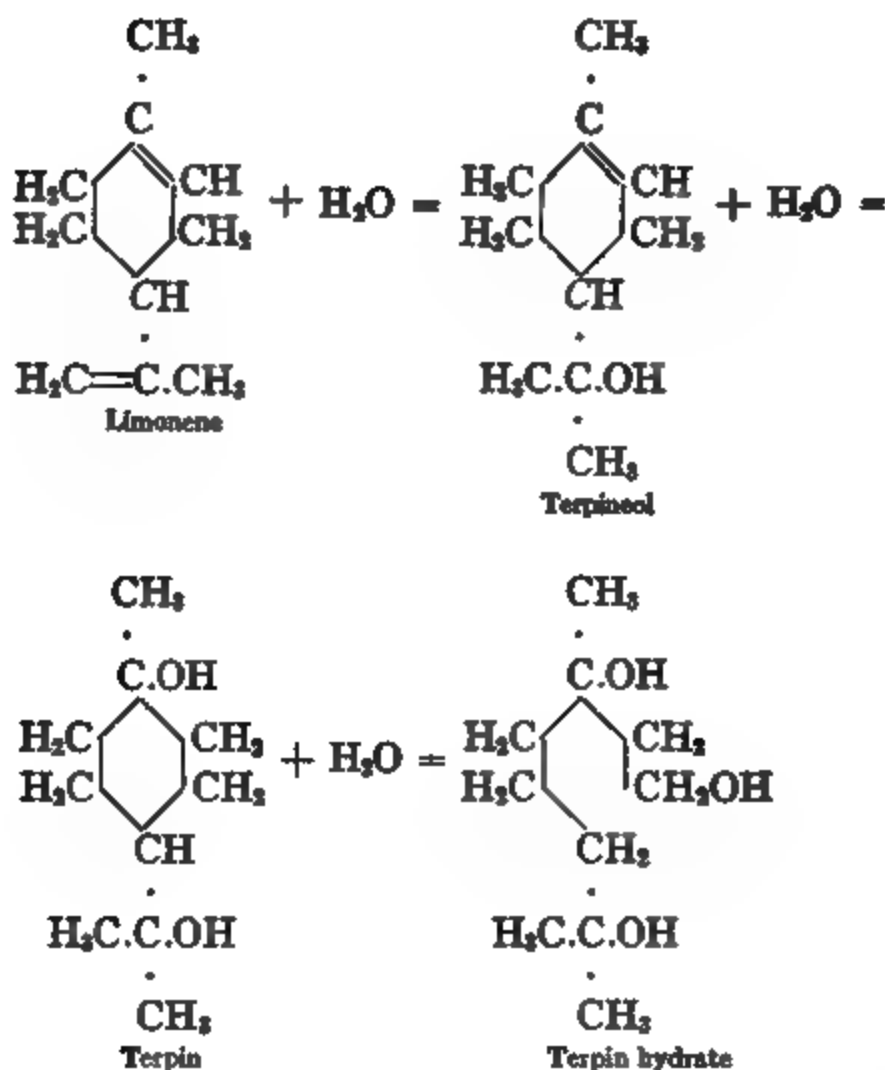


and the position of a double bond between two or more carbon atoms, as in the formula of limonene given above, is indicated by the Greek letter  $\Delta$  with the numbers of the carbon atoms between which the double bonds occur as exponents. Thus, limonene is  $\Delta^{1,8(9)}$  menthadiene.

Hexahydro-*p*-cymene is designated *menthane*, as it is a saturated hydrocarbon and can be readily obtained by the reduction of its hydroxyl derivative, menthol. It is not a natural product, but is made from *p*-cymene by passing its vapor mixed with hydrogen over finely divided nickel heated to  $180^\circ$ . It is a liquid boiling at  $168^\circ$ – $169^\circ$ .

**Limonene** (carvene, citrene),  $\text{C}_{10}\text{H}_{16}$ , occurs very widely distributed in nature both in the dextro- and levo- forms and in the *dl*-form, which is called dipentene. *d*-Limonene occurs most abundantly in the oils of orange, lemon, bergamot, mandarin, and in a number of other oils. *l*-Limonene occurs in pine needle oil, in pine cone oil and in other oils. Both limonenes are liquids of an agreeable lemon-like odor, boiling at  $175^\circ$ – $176^\circ$ . They yield the same derivatives, which differ only in the direction in which they rotate polarized light. When equal quantities of *d*- and *l*-limonene are mixed, dipentene is formed, and dipentene also results when either of the limonenes is heated to a high temperature or when they are heated with acids. In the cold, acids frequently cause the hydration of limonene to terpineol and terpin hydrate: —

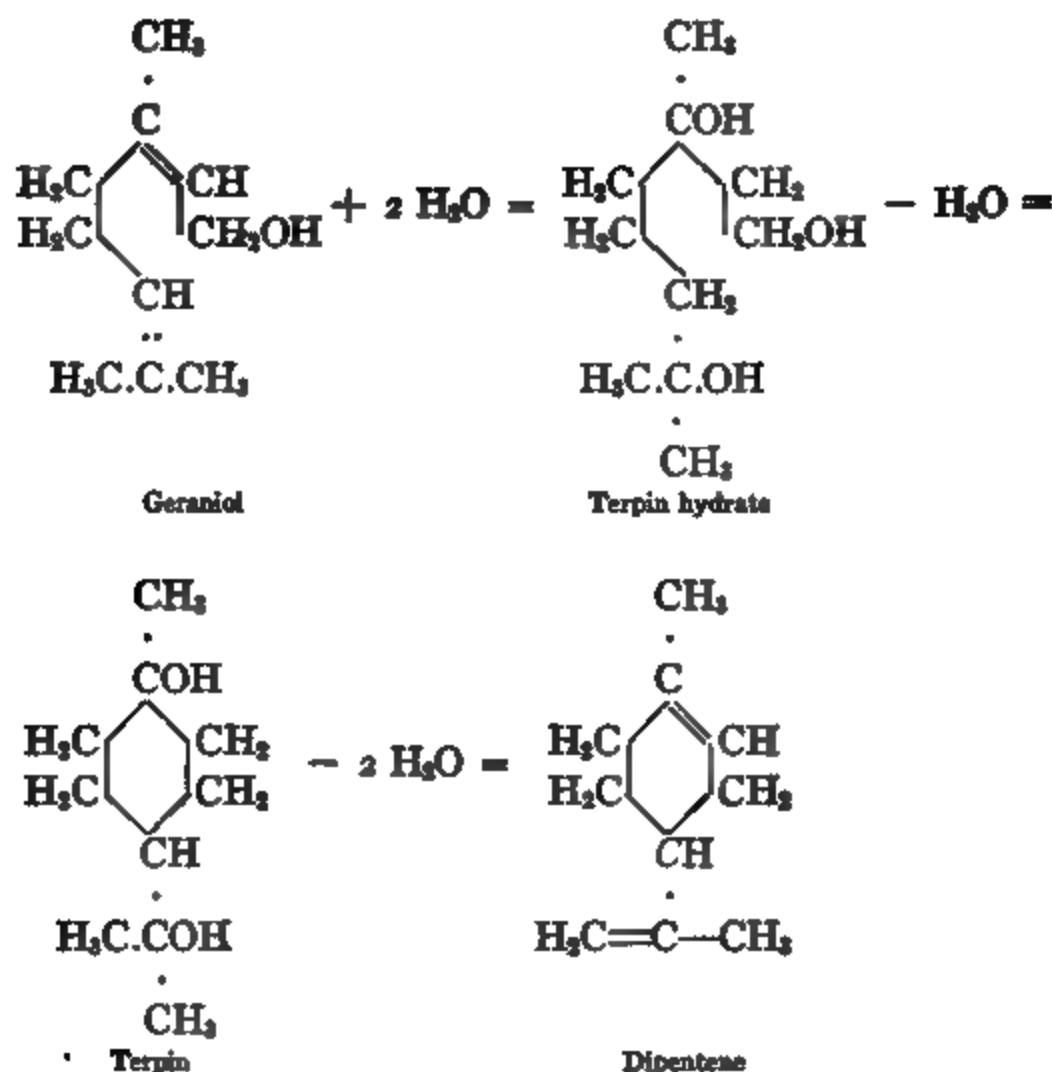




Concentrated sulphuric acid changes limonene to *p*-cymene. The limonenes take up four atoms of bromine and yield optically active tetrabromides that melt at  $104^\circ$ – $105^\circ$ . They also take up two molecules of hydrochloric acid, forming, however, a dihydrochloride of dipentene, melting at  $50^\circ$ .

**Dipentene** (inactive limonene), occurs frequently in nature and is found in Swedish turpentine oil and in a number of other volatile oils.

It has been made synthetically by the polymerization of isoprene (444), and it is formed together with isoprene when caoutchouc is distilled. It results also when pinene, limonene, and phellandrene are heated to  $250^\circ$ – $300^\circ$ . Its synthesis from the alcohols, linalool and geraniol (459) determines its structure and that of the limonenes:—



This change is brought about by shaking with dilute sulphuric acid.

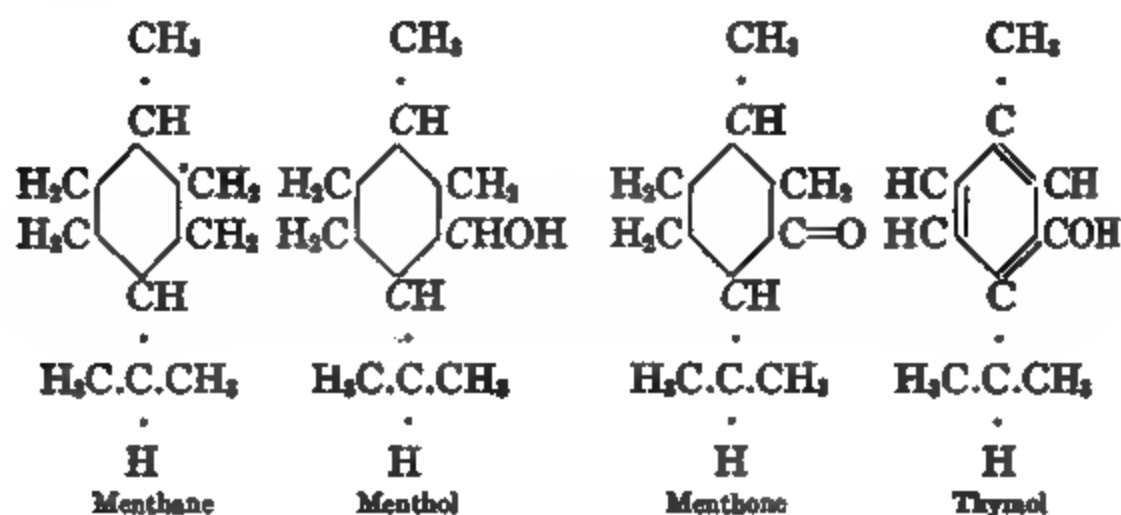
NOTE FOR STUDENT. — Does the formula for dipentene contain an asymmetric carbon atom?

Dipentene differs from limonene only in being optically inactive and in giving optically inactive derivatives.

### *Monocyclic Alcohols and Ketones*

**Menthol**,  $\text{C}_{10}\text{H}_{19}\text{OH}$  (peppermint camphor), is present in the peppermint oils, of which *l*-menthol is the principal constituent together with its acetate and isovalerate. On cooling, menthol separates from the oil of peppermint in colorless, hexagonal needles having the characteristic odor of oil of peppermint. It

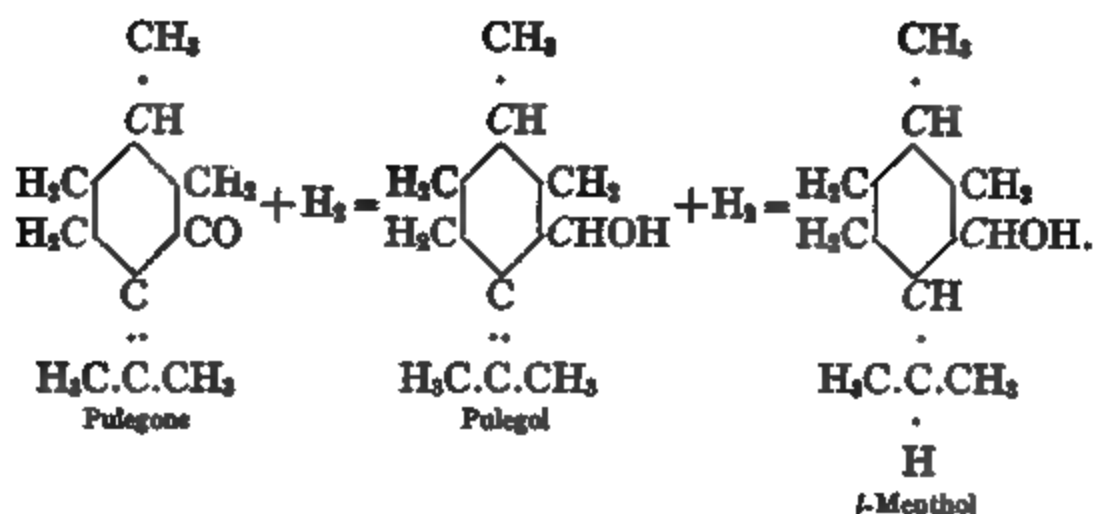
melts between  $43.5^{\circ}$  and  $44.5^{\circ}$ , and boils at  $215.5^{\circ}$ . It is used as an antiseptic and anæsthetic. When heated with copper sulphate it gives *p*-cymene. Menthol is a saturated, secondary alcohol derived from menthane, as it yields menthane (hexahydro-*p*-cymene) on reduction with hydriodic acid and phosphorus, and the ketone, menthone, on oxidation with chromic acid:—



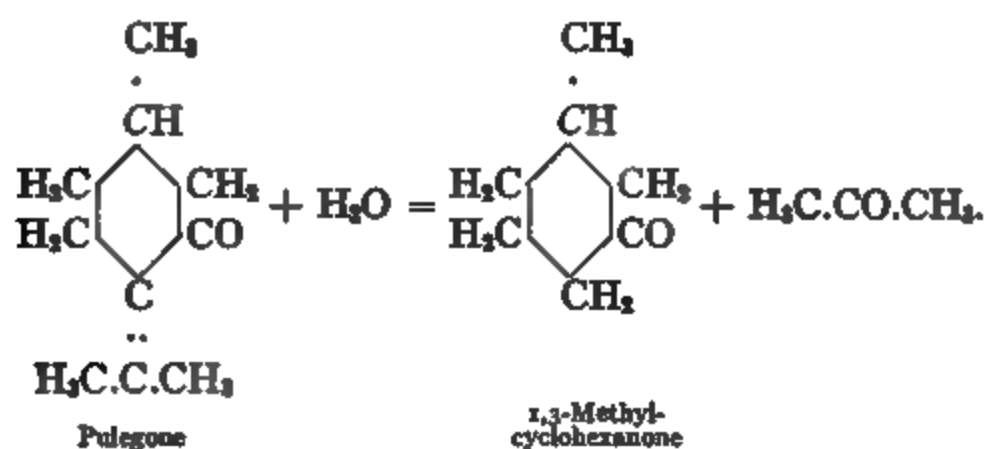
The position of the OH group is determined by the fact that when menthone in chloroform solution is treated with bromine it gives a crystalline dibromomenthone,  $\text{C}_{10}\text{H}_{16}\text{Br}_2\text{O}$  (m.p.  $79^{\circ}$ – $80^{\circ}$ ) from which, by heating with quinoline, thymol (see above) is formed. Menthol is made artificially by the reduction of menthone and of pulegone. (See below.)

**d-Pulegone**,  $\text{C}_{10}\text{H}_{16}\text{O}$ , occurs in European pennyroyal oil and also in other labiate oils, sometimes together with menthol and menthone. It is a colorless liquid having a sweetish, peppermint-like odor, resembling that of menthone. It boils at  $224^{\circ}$ .

It is an unsaturated ketone, as it combines with bromine to form a liquid dibromide and with a molecule of hydrobromic acid to form a crystalline hydrobromide, and forms a semicarbazone with semicarbazide. When reduced in alcoholic solution with sodium it gives, first, the corresponding secondary alcohol, *pulegol*, and then *l*-menthol:—



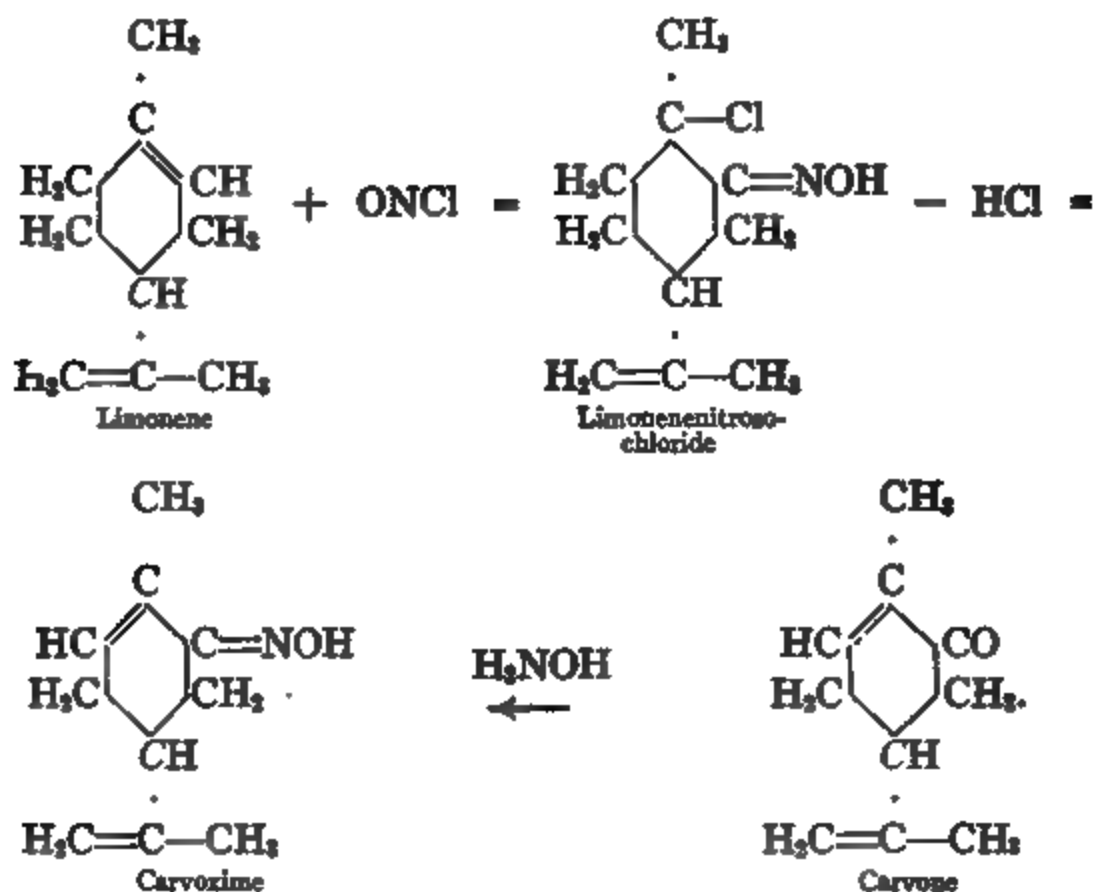
When reduced with hydrogen at  $180^\circ$ , nickel being used as a catalyst, pulegone gives menthone. When it is superheated with water pulegone gives acetone and 1,3-methylcyclohexanone :—



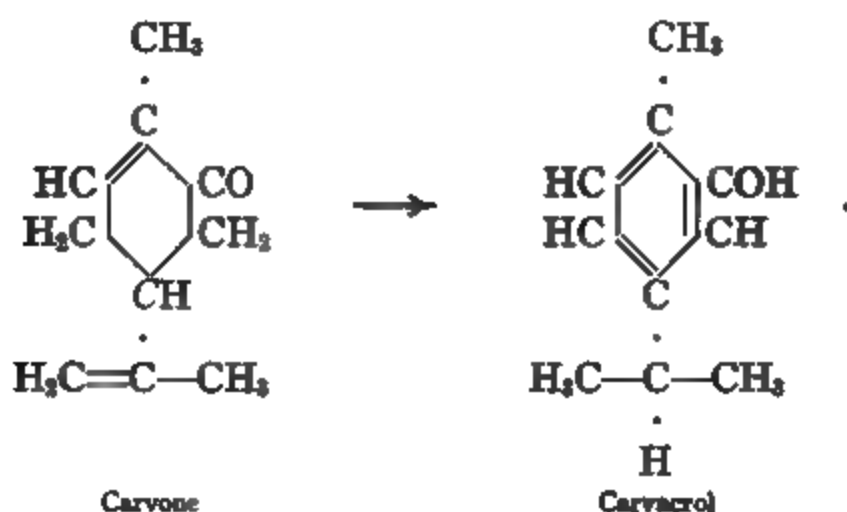
This reaction determines the position of the double bond in pulegone.

*d*-Carvone,  $\text{C}_{10}\text{H}_{14}\text{O}$ , is present in the oil of caraway and in dill oil, of which it constitutes from 50 to 60 per cent. It is a colorless liquid having the odor of the oil of caraway and boiling at  $230^\circ$ – $231^\circ$ . It is an unsaturated ketone and forms an oxime with hydroxylamine.

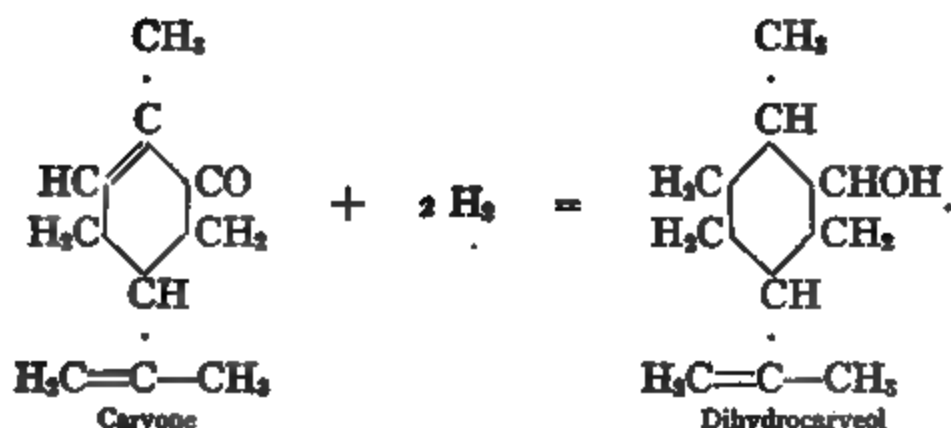
This oxime also results when limonene is treated with nitrosyl chloride, and hydrochloric acid is eliminated from the addition product thus formed :—



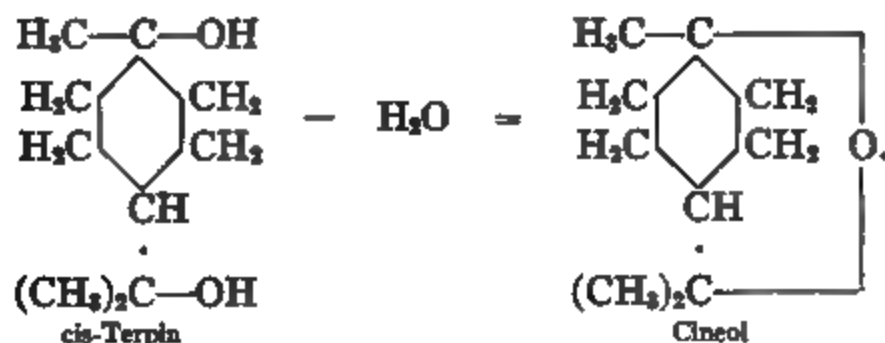
When heated with phosphoric acid or with solutions of the alkalis carvone is converted into carvacrol (383), and this reaction determines the position of the oxygen atom : —



When treated in alcoholic solution with sodium, carvone is not reduced to carveol,  $\text{C}_{10}\text{H}_{15}\text{OH}$ , but takes up four atoms of hydrogen to form dihydrocarveol : —



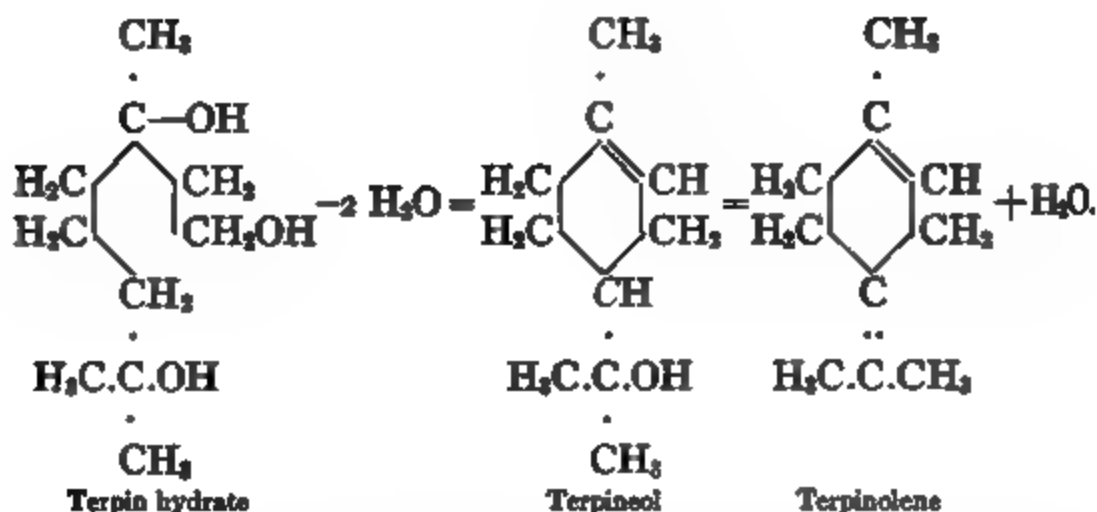
**Cineol** (eucalyptol),  $\text{C}_{10}\text{H}_{18}\text{O}$ , is very widely distributed in nature. It is the principal constituent of the oil of *Eucalyptus globulus*, of cajeput oil, niaouli oil and of the oil of wormwood (*Oleum cinæ*), and is found in a very large number of other oils. It is a colorless liquid, optically inactive, and has an odor resembling that of camphor. It solidifies at about  $1^\circ$  and boils at  $176^\circ$ – $177^\circ$ . The oxygen in cineol is not present in the form of hydroxyl or as a ketone group, since sodium does not act upon it and it does not react with either hydroxylamine or phenylhydrazine. Since it is formed by the elimination of a molecule of water from *cis*-terpin it is regarded as an oxide: —



**NOTE FOR STUDENT.** — Does cineol contain an asymmetric carbon atom?

Cineol has basic properties and forms oxonium salts with hydrochloric and other acids.

**Terpineol**,  $\text{C}_{10}\text{H}_{18}\text{O}$ , occurs in the *d*-form in the oil of orange and in the *l*-form in lignaloe oil. The commercial liquid, terpineol, is formed by the action of dilute sulphuric acid on terpin hydrate: —



The  $\alpha$ -terpineol is a solid melting at  $35^\circ$  and boiling at  $217^\circ$ – $218^\circ$ . The commercial liquid product, which is a mixture of isomers, has an odor resembling that of the lilac, and is used in perfumery. When the optically active terpeneols are boiled with a solution of oxalic acid they lose a molecule of water and give optically inactive terpinolene, as shown above.

NOTE FOR STUDENT. — Does the formula for terpinolene contain an asymmetric carbon atom? Does that of terpeneol?

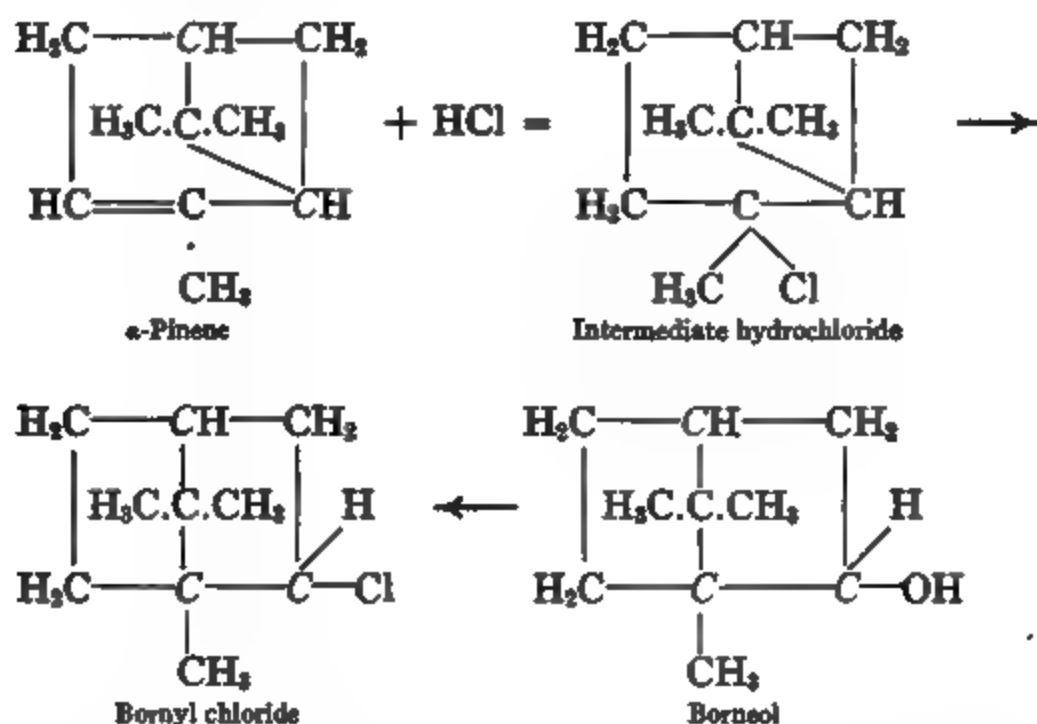
### BICYCLIC TERPENES

The two most important members of this group are pinene and camphene.

$\alpha$ -Pinene,  $\text{C}_{10}\text{H}_{16}$ , is remarkably widely distributed in nature and occurs in the *d*-, *l*-, and *dl*-forms. It forms the principal constituent of the distillate from the oleoresins obtained from several species of pine, and known commercially as turpentine oils. French and Spanish turpentine consist for the most part of *l*- $\alpha$ -pinene, while in the Greek and American oil the *d*- $\alpha$ -pinene forms the largest part. There are also American turpentines which are levo rotatory or nearly inactive. It is a colorless, mobile liquid boiling at  $155^\circ$ – $156^\circ$ . Like most of the terpenes,  $\alpha$ -pinene takes up oxygen from the air and partly resinifies. It is very readily converted into other terpenes. When heated to  $250^\circ$ – $270^\circ$  it is changed to dipentene, and it is converted into

terpinolene by means of alcoholic sulphuric acid.  $\alpha$ -Pinene is an unsaturated hydrocarbon with one double bond. When dry hydrochloric acid gas is passed into the well-cooled and dried  $\alpha$ -pinene one molecule of hydrochloric acid is taken up and bornyl chloride results.

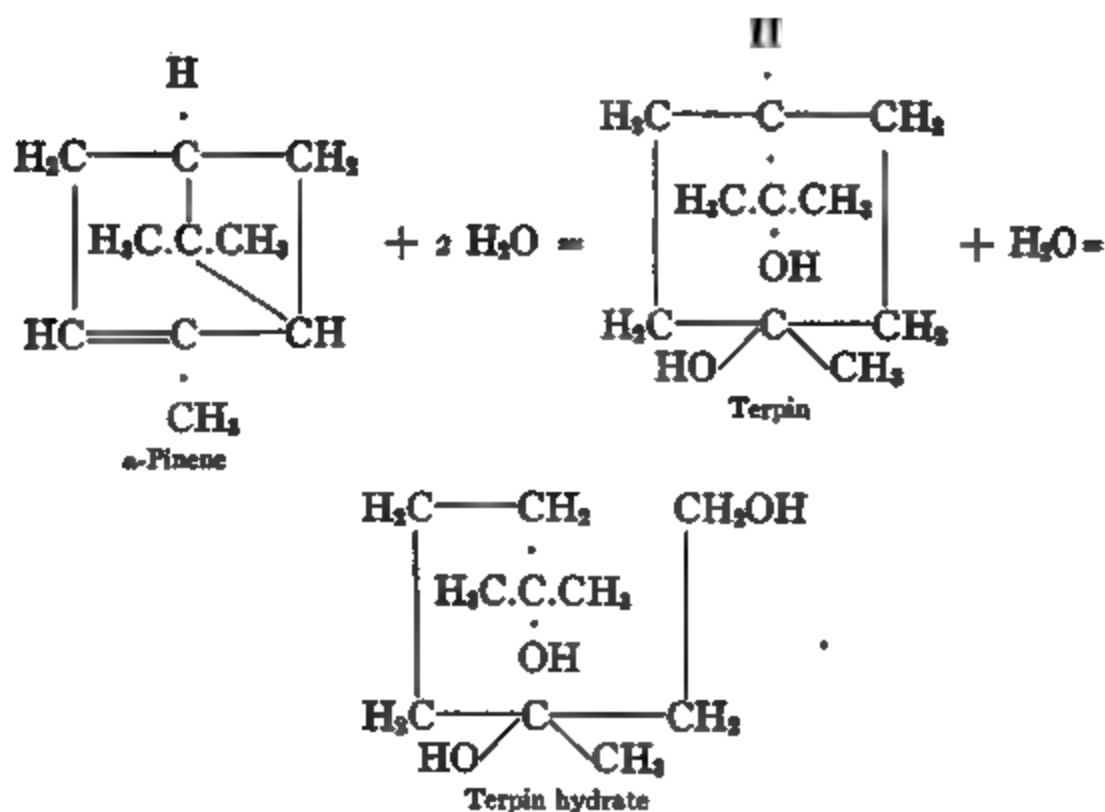
This substance used to be called pinene hydrochloride,  $C_{10}H_{16}HCl$ , and on account of its odor, which resembles that of natural camphor, "artificial camphor." It is also made from borneol (455) by the action of phosphorus pentachloride or by the action of hydrochloric acid, and hence arose the name:—



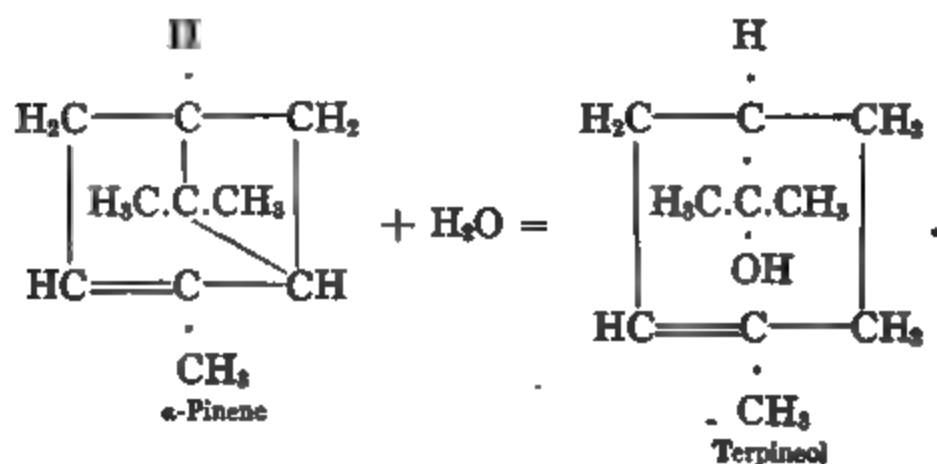
The formula now given to  $\alpha$ -pinene represents it as containing a hexamethylene and a tetramethylene ring. It will be seen from the above formulas that in the conversion into bornyl chloride molecular rearrangement takes place with the formation of the more stable pentamethylene ring. When bornyl chloride is heated with aniline it gives camphene.

**Terpin hydrate**,  $C_{10}H_{18}(OH)_2 + H_2O$ , is formed very readily from oil of turpentine by allowing it to stand for several days with dilute sulphuric acid:—



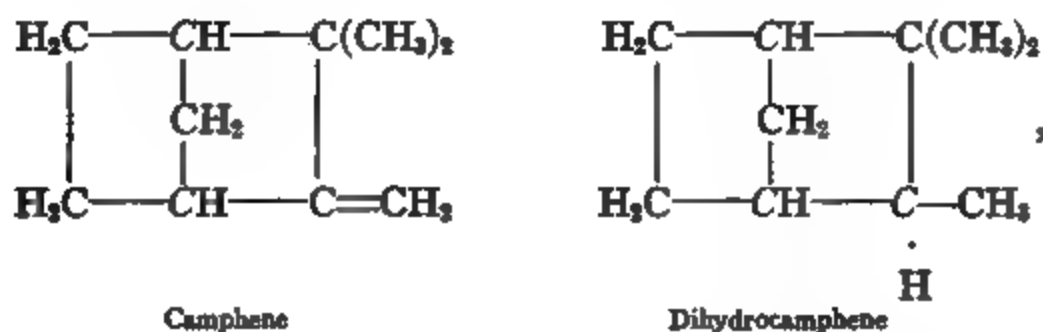


Terpin hydrate is made in this way on the large scale, and is converted into the liquid terpeneols by the action of dilute sulphuric acid for use in perfumery. When heated in acetic acid solution with benzenesulphonic acid  $\alpha$ -pinene takes up only one molecule of water, breaking the tetramethylene ring and forming terpeneol:—



This reaction establishes the position of the double bond in  $\alpha$ -pinene.

**Camphene**,  $C_{10}H_{16}$ , is the only solid hydrocarbon of this formula occurring in nature. Both the *d*- and the *l*-forms have been found in the oils of lemon and other volatile oils. Artificially camphene is obtained from bornyl chloride (made from pinene or from borneol) by the elimination of hydrochloric acid (453). It forms a colorless crystalline mass having a faint camphor-like odor and it sublimes very readily. It is much more stable towards light and air than the other terpenes. It melts at about  $50^{\circ}$  and boils at about  $160^{\circ}$ . The structural formula for camphene,

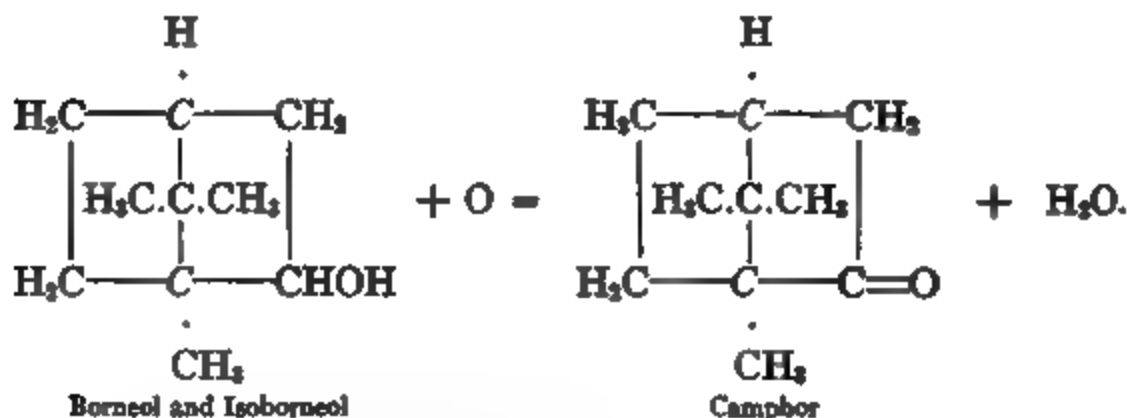


is in accord with the fact that it forms a dibromide,  $C_{10}H_{16}Br_2$  (m.p.  $91^{\circ}$ – $91.5^{\circ}$ ), and combines with one molecule of hydrochloric acid. On reduction with hydrogen in the presence of platinum it gives dihydrocamphene (see above) isomeric with camphene (456). When it is heated with glacial acetic acid and 50 per cent sulphuric acid for 2–3 hours at  $50^{\circ}$ – $60^{\circ}$  it is converted into isobornyl acetate, from which isoborneol (457) can be obtained by saponification. On oxidation with chromic acid camphene is converted into camphor.

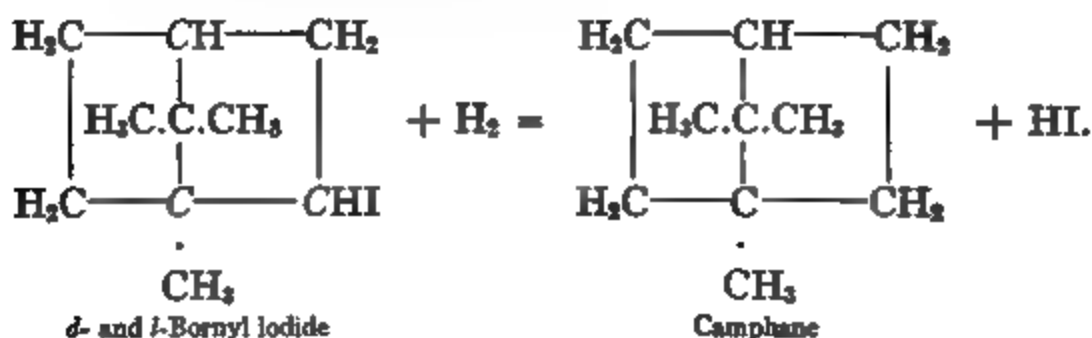
### *Bicyclic Alcohols and Ketones*

**Borneol**, **Borneo camphor**,  $C_{10}H_{18}O$ , from the camphor tree (*Dryobalanops camphora*) growing in Borneo, Sumatra, etc., is the *d*-form. The Ngai camphor consists of the *l*-borneol. Both forms are present also in various volatile oils. The artificial borneol obtained by the reduction of *d*- or *l*-camphor in alcoholic solution by sodium is a mixture of *d*- or *l*-borneol and its stereoisomer isoborneol. The pure *d*-borneol crystallizes in

hexagonal plates that melt at  $203^{\circ}$ – $204^{\circ}$  and boil at  $212^{\circ}$ . Like camphor it volatilizes at ordinary temperatures. It has an odor similar to that of camphor and ambra. It is a saturated, secondary alcohol and gives the saturated ketone, camphor, on oxidation: —



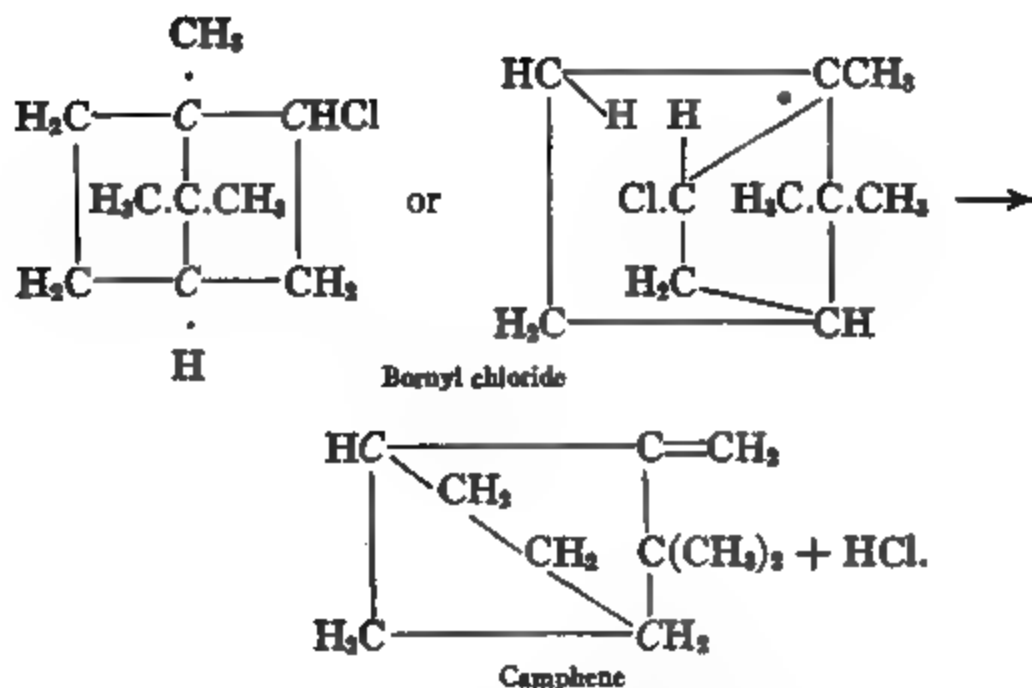
Borneol gives optically active bornyl iodide with hydriodic acid (identical with pinene hydroiodide) and this when reduced with zinc dust and hydriodic acid in glacial acetic acid yields the optically *inactive* camphane: —



The optically inactive camphane is obtained from both *d*- and *l*-bornyl iodide.

NOTE FOR STUDENT. — Does camphane contain an asymmetric carbon atom? Explain the fact that borneol and isoborneol both give camphor on oxidation and that camphor on reduction gives both borneol and isoborneol. What does fructose give on reduction?

With phosphorus pentachloride borneol gives bornyl chloride, identical with  $\alpha$ -pinene hydrochloride (453), and this gives camphene when boiled with aniline: —

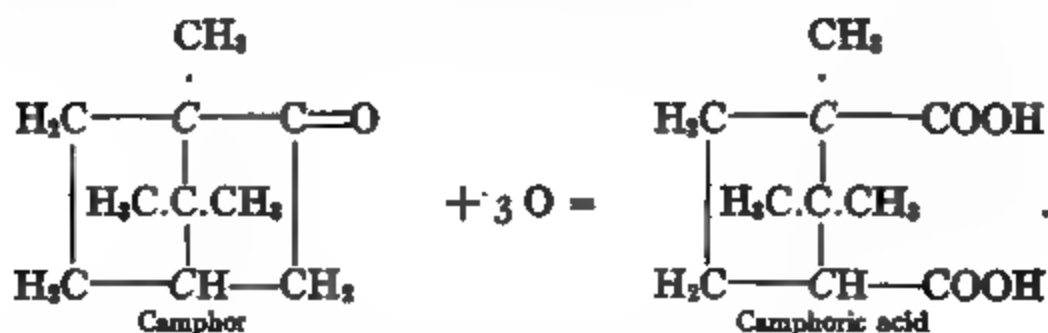


**Isoborneol** is always formed together with borneol in the reduction of camphor. It is easily obtained from camphene in the form of its acetic acid ester, isobornyl acetate, by warming it to  $50^\circ$ – $60^\circ$  for some hours with glacial acetic acid and 50 per cent sulphuric acid. On saponification of the ester isoborneol results. This crystallizes in leaflets of the hexagonal system, which melt at  $212^\circ$  in a sealed tube. It volatilizes very readily and is more soluble than borneol. Isobornyl chloride is identical with camphene hydrochloride. Like borneol, isoborneol is a saturated secondary alcohol, and gives camphor on oxidation. Hence, it is a stereoisomer of borneol. It differs from borneol in its action towards dehydrating agents, such as zinc chloride. Borneol is very stable, while isoborneol yields camphene.

**d-Camphor**,  $\text{C}_{10}\text{H}_{16}\text{O}$ , generally called Japanese or laurus camphor to distinguish it from Borneo camphor, is obtained on the large scale together with camphor oil by distilling the finely cut wood of the *Cinnamomum camphora* with steam. It has also been found in several volatile oils. The *l*- and *dl*-forms likewise occur in some volatile oils. Both *d*- and *l*-camphor are formed artificially by the oxidation of the corresponding optically active borneols with nitric acid or of camphene with chromic acid. Camphor crystallizes in the hexagonal system. It has a

characteristic odor and sublimates even at ordinary temperatures. It melts at  $175^{\circ}$ , boils at  $204^{\circ}$ , and is readily soluble in organic solvents. Small pieces of camphor when placed on water rotate in a very lively manner.

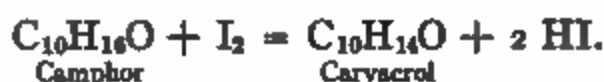
Camphor is a saturated ketone. It yields an oxime with hydroxylamine, and on reduction in alcoholic solution with sodium it gives both borneol and isoborneol (456). Oxidized with nitric acid it gives the dibasic camphoric acid:—



Phosphorus pentoxide converts camphor into *p*-cymene:—



while the action of iodine results in the formation of carvacrol:—



As the hydroxyl group in carvacrol (383) is in the ortho position to the methyl group, it follows that the ketone group in camphor is also ortho to the methyl group.

Approximately 9 million pounds of camphor are produced annually. Two-thirds of this is used in the celluloid industry (in the manufacture of celluloid articles, motion-picture films, etc.); the rest is used in the manufacture of smokeless powder, explosives, and for disinfection and medicinal purposes. Camphor is now manufactured artificially from the oil of turpentine. The pinene is first converted into bornyl chloride by the action of dry hydrochloric acid, and the bornyl chloride is then heated with bases. This gives camphene. The camphene is then converted into camphor by oxidation with chromic acid mixture, in which case bornyl and isobornyl chromates are formed as intermediate products. Another method

converts camphene into isobornyl acetate (457), and this is hydrolyzed to isoborneol, which on oxidation gives camphor (456). The synthetic camphor is optically inactive.<sup>1</sup>

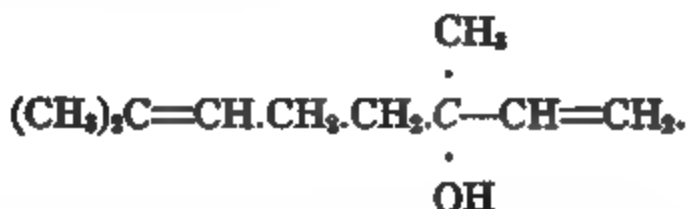
Isomeric with camphor or borneol are three important substances, *geraniol*, *linalool*, and *geranial*, which are termed olefine camphors, to distinguish them from camphor and borneol.

**Geraniol**,  $C_{10}H_{18}O$ , is the principal constituent of palmarosa oil and of the German and Turkish rose oils. It is also found in considerable quantities in the oils of geranium, citronella, and lemon grass. Pure geraniol is a colorless oily liquid with a pleasant rose-like odor, that boils at  $229^{\circ}$ – $230^{\circ}$ . It is optically inactive and is a primary alcohol, as it gives geranial,  $C_{10}H_{16}O$ , an aldehyde, on oxidation, and has been made by the reduction of this aldehyde. It has been shown to have the structure:—



It yields anhydrogeraniol,  $C_{10}H_{16}$  (see above), when heated with dehydrating agents, and is converted into dipentene by the action of dilute sulphuric acid (447).

**Linalool**,  $C_{10}H_{18}O$ , is isomeric with geraniol and forms the chief constituent of linaloe oil. It boils at  $198^{\circ}$ – $199^{\circ}$  and is readily converted into geraniol by the action of organic acids. It is optically active and is a tertiary alcohol. It has been shown to have the structure:—



<sup>1</sup> See article on Camphor in Thorpe's *Dictionary of Applied Chemistry*, latest edition.

Both geraniol and linalool are very readily converted into the terpenes and their oxygen derivatives (447).

**Geranial, citral**,  $C_{10}H_{16}O$ , is the chief constituent of lemon grass oil. It is a light yellow liquid, optically inactive, having the odor of lemon. It boils at  $110^{\circ}$  to  $111^{\circ}$  (12 mm.). As it gives geraniol when reduced, and geranic acid, containing the same number of carbon atoms, when oxidized, it has the following structure:—



Citral

When heated with potassium hydrogen sulphate citral is converted into *p*-cymene. Citral readily condenses with acetone to form *ionone*,  $C_{15}H_{20}O$ , which has the odor of violets and is manufactured on the large scale.<sup>1</sup>

### POLYTERPENES

**Caoutchouc**,  $(C_5H_8)_x$ , generally known as rubber or indiarubber, is the coagulated latex or milky juice of certain tropical plants, especially of *Hevea Braziliensis*. It can be obtained pure, in the form of a white, amorphous mass, by dissolving the crude product in benzene, precipitating with alcohol and extracting this product with acetone. Analyses of this product give results agreeing with the formula,  $C_5H_8$ . Rubber is a colloid of high molecular weight belonging to the class of terpenes. It combines with bromine to form a tetrabromide  $(C_{10}H_{16}Br_4)_x$ , and with hydrochloric acid to form a dihydrochloride  $(C_{10}H_{16} \cdot 2 HCl)_x$ . When heated with a small amount of sulphur under pressure or when treated with sulphur chloride in the cold, it undergoes *vulcanization*. This process of vulcanization by heating with sulphur is much facilitated by the presence of accelerators (such as lead oxide, zinc oxide, thiocarbanilide, etc.). It increases the strength, elasticity, durability, and usefulness of

<sup>1</sup> See *Volatile Oils*, by E. Gildemeister, 2d ed., translated by E. Kremers, page 464.

rubber. Unvulcanized rubber becomes sticky at  $30^{\circ}$  and loses its elasticity completely at  $0^{\circ}$ . When heated with a larger amount of sulphur and to a higher temperature, *hard rubber*, ebonite or vulcanite is formed.

When crude rubber is subjected to dry distillation both isoprene (444) and dipentene are formed, and an artificial rubber has been made by the polymerization of isoprene by heat and other polymerizing agents. This artificial rubber can be vulcanized like the natural rubber. Owing to the great commercial importance of rubber many attempts have been made to prepare it artificially by the polymerization of isoprene, but so far the process has not been a commercial success and the production of an artificial rubber completely identical in all its properties with the natural product has not yet been attained. The world's production of plantation rubber in 1920 was 304,000 tons.<sup>1</sup> The value of the rubber industry in 1919 was \$1,122,000,000. Gutta percha and balata seem to be isomeric with rubber.

<sup>1</sup> See article on Rubber in Thorpe's *Dictionary of Applied Chemistry* and in *J. Ind. and Eng. Chem.*, May, 1922.



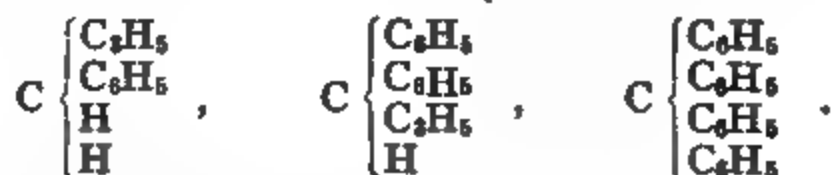
## CHAPTER XVI

### DIPHENYLMETHANE, TRIPHENYLMETHANE, TETRA-PHENYLMETHANE, AND THEIR DERIVATIVES

As we have seen, toluene may be regarded either as methylbenzene or phenylmethane. Of course, according to all that is known regarding similar substances, the two views are identical. Regarding it, for our present purpose, as phenylmethane,

we may write its formula thus:  $C \begin{Bmatrix} C_6H_5 \\ H \\ H \\ H \end{Bmatrix}$ .

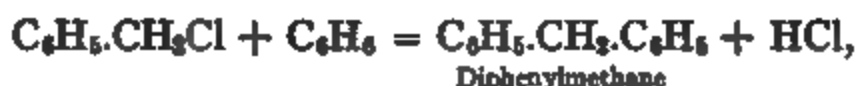
This suggests the possibility of the existence of such substances as *Diphenylmethane*, *Triphenylmethane*, and *Tetraphenylmethane*:—



All these hydrocarbons are known. The derivatives of di- and triphenylmethane are of special interest and importance. Only di- and triphenylmethane will be treated of here.

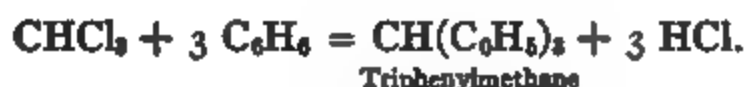
There is one reaction by means of which these hydrocarbons can be made very readily. It has also been used for the synthesis of many other aromatic hydrocarbons and their derivatives. It depends upon the remarkable fact that, when an aromatic hydrocarbon is brought together with a compound containing chlorine, and anhydrous aluminium chloride then added, hydrochloric acid is evolved, and union of the two residues is effected, the aluminium chloride not entering into the composition of the product (Friedel-Crafts reaction). Thus, when benzene and benzyl chloride,  $C_6H_5 \cdot CH_2Cl$ , are brought together, no action takes

place; but, if some anhydrous aluminium chloride is added, reaction takes place according to the following equation:—



and diphenylmethane is formed.

Similarly, when chloroform and benzene are brought together in the presence of aluminium chloride, triphenylmethane is formed according to this equation:—



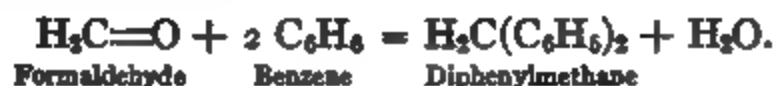
Another method by which these hydrocarbons can be made, consists in heating a chloride and a hydrocarbon together in the presence of zinc dust. Thus, benzyl chloride and benzene give diphenylmethane when boiled with zinc dust; and benzal chloride,  $\text{C}_6\text{H}_5\cdot\text{CHCl}_2$ , and benzene give triphenylmethane:—



Diphenylmethane,  $\text{H}_2\text{C}(\text{C}_6\text{H}_5)_2$ , is most readily made from benzyl chloride, benzene, and aluminium chloride. It can also be obtained from methylene chloride and benzene in the presence of aluminium chloride:—



Diphenylmethane and its homologues are also formed from the aliphatic aldehydes and the aromatic hydrocarbons by the action of concentrated sulphuric acid:—



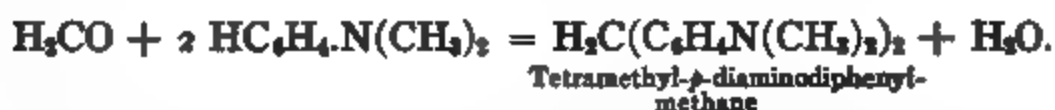
Acetic aldehyde gives diphenylethane,  $\text{H}_3\text{C}\cdot\text{CH}(\text{C}_6\text{H}_5)_2$ . Diphenylmethane crystallizes in colorless needles that have the odor of oranges and melt at  $26^\circ$ . It is readily soluble in alcohol and ether and distils at  $262^\circ$ .

***p*-Diaminodiphenylmethane**,  $(\text{H}_2\text{NC}_6\text{H}_4)_2\text{CH}_2$ , is obtained by heating anhydroformaldehydeaniline,  $\text{C}_6\text{H}_5\text{N}=\text{CH}_2$  (made by the action of formaldehyde on aniline), with aniline and aniline salt. *Anhydro-*p*-aminobenzyl alcohol*,  $\text{H}-\text{N}-\text{C}_6\text{H}_4-\text{CH}_2$ ,

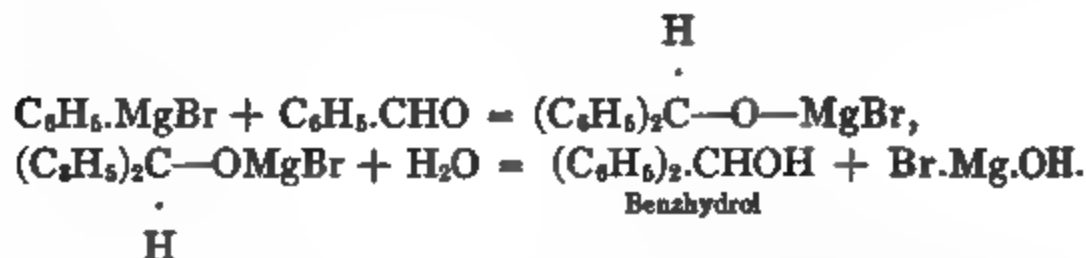
is formed as the intermediate product:—



It is used in the preparation of fuchsine (469). Its *tetramethyl* derivative is obtained from dimethylaniline and formaldehyde:—



**Benzhydrol**, diphenylcarbinol,  $(\text{C}_6\text{H}_5)_2\text{CHOH}$ , is made from diphenylmethyl bromide,  $(\text{C}_6\text{H}_5)_2\text{CHBr}$  (from diphenylmethane and bromine), by heating with water. It is also formed by the reduction of benzophenone (400) and gives benzophenone on oxidation. It can also be obtained by the action of phenyl magnesium bromide on benzaldehyde:—



**Tetramethyl-*p*-diaminobenzhydrol**,  $((\text{CH}_3)_2\text{NC}_6\text{H}_4)_2\text{CHOH}$ , is obtained by the oxidation of tetramethyl-*p*-diamino-diphenylmethane and also by the reduction of Michler's ketone (401). It crystallizes in colorless prisms, which dissolve in glacial acetic acid with an intense blue color. It is known as Michler's hydrol, and is used in the synthesis of many dyestuffs.

**Triphenylmethane**,  $\text{CH}(\text{C}_6\text{H}_5)_3$ .—This hydrocarbon can be made, as above described, from benzal chloride and benzene, and from chloroform and benzene. It is best obtained from triphenylmethyl chloride (made from carbon tetrachloride,

benzene, and aluminium chloride) by the action of zinc dust and glacial acetic acid:—



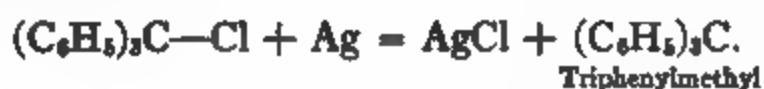
It forms lustrous, thin laminæ, that melt at  $93^\circ$ . It is insoluble in water; easily soluble in benzene, ether, and chloroform. It is crystallized best from hot alcohol.

With bromine triphenylmethane gives *triphenylmethyl bromide*,  $(\text{C}_6\text{H}_5)_3\text{C—Br}$ , and this is converted into *triphenylcarbinol*,  $(\text{C}_6\text{H}_5)_3\text{C—OH}$ , by simply boiling with water. Triphenylcarbinol melts at  $159^\circ$ . It can also be prepared by the oxidation of triphenylmethane in glacial acetic acid solution with chromic acid. It has been made synthetically from benzophenone by the action of phenyl magnesium bromide:—



On reduction with zinc and acetic acid it is converted into triphenylmethane.

Triphenylmethyl,  $(\text{C}_6\text{H}_5)_3\text{C}$ , is the name given to a compound obtained by Gomberg by the action of molecular silver on triphenylmethyl chloride in solution in benzene:—

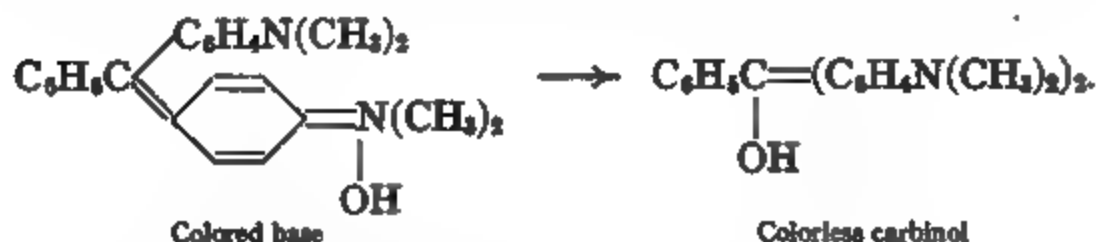


It is characterized by its remarkable chemical activity. It combines at once with oxygen when brought in contact with the air to form the colorless *peroxide*,  $(\text{C}_6\text{H}_5)_3\text{CO—OC}(\text{C}_6\text{H}_5)_3$ , and unites quantitatively with iodine to form triphenylmethyl iodide,  $(\text{C}_6\text{H}_5)_3\text{CI}$ . Molecular weight determinations by the freezing point method show that it has the formula,  $(\text{C}(\text{C}_6\text{H}_5)_3)_2$ . According to this it is hexaphenylethane,  $(\text{C}_6\text{H}_5)_3\text{C—C}(\text{C}_6\text{H}_5)_3$ . When first dissolved in benzene the solution is colorless, but it soon becomes orange-yellow. When this solution is shaken with air the color disappears, owing to the formation of the peroxide, but it reappears when the solution is allowed to stand.

Tetramethyldiaminotriphenylmethane, *leucomalachite green*,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2$ , is formed when benzaldehyde and



When a solution of sodium hydroxide is added to a solution of malachite green, the colorless tetramethyldiaminotriphenylcarbinol is precipitated, as the colored base first formed is unstable and goes over into the colorless carbinol, which is insoluble in water:—

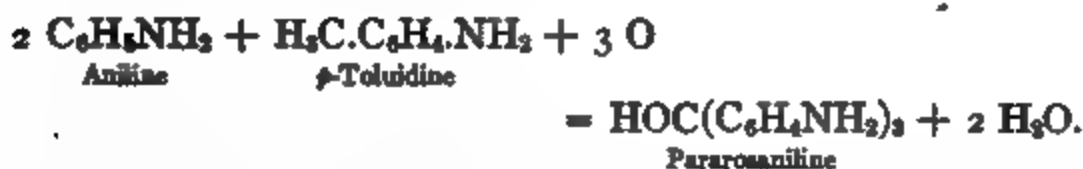


Somewhat over 654,000 pounds of malachite green (oxalate) were made in the United States in 1920.

*p*-Trinitrotriphenylmethane,  $\text{HC}(\text{C}_6\text{H}_4\text{NO}_2)_3$ , is formed by treating triphenylmethane with fuming nitric acid. It crystallizes in scales that melt at  $203^\circ$ . On reduction it gives *triaminotriphenylmethane*,  $\text{HC}(\text{C}_6\text{H}_4\text{NH}_2)_3$ , which is called *para-leucaniline*, as it is also formed by the reduction of *pararos-aniline*,  $\text{HOC}(\text{C}_6\text{H}_4\text{NH}_2)_3$ , and is converted into pararosaniline on oxidation. It crystallizes in leaflets that melt at  $148^\circ$ . When trinitrotriphenylmethane is oxidized with chromic acid it gives trinitrotriphenylcarbinol,  $\text{HOC}(\text{C}_6\text{H}_4\text{NO}_2)_3$ , and when this is reduced with zinc dust and acetic acid, pararosaniline is formed.

### TRIPHENYLMETHANE DYES

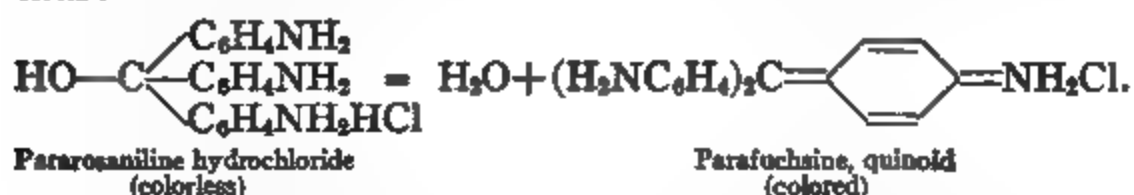
Many of the triphenylmethane dyes are salts of pararos-aniline,  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}$ , and of its homologue, rosaniline,  $\text{C}_{19}\text{H}_{19}(\text{CH}_3)\text{N}_3\text{O}$ , and their derivatives. Pararosaniline is formed when aniline and paratoluidine are oxidized with arsenic acid or with nitrobenzene:—



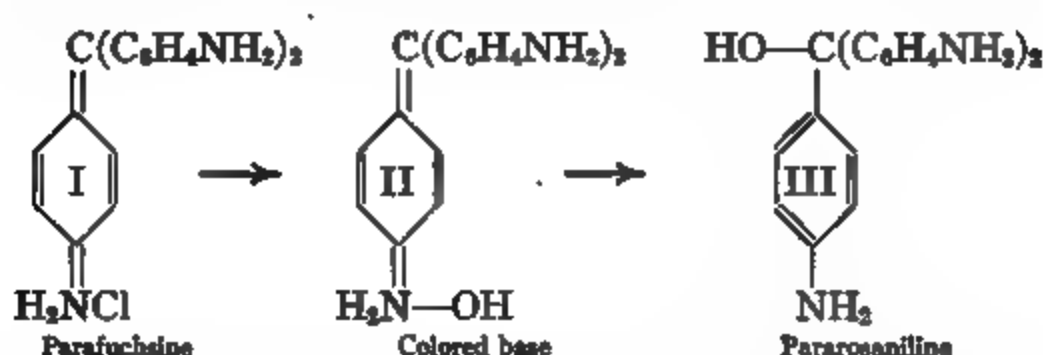
Rosaniline is formed by oxidizing aniline and a mixture of ortho and paratoluidine:—



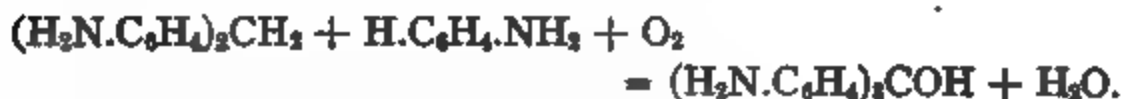
In the commercial preparation of *fuchsine* or *magenta*, a mixture of aniline, ortho- and paratoluidine is oxidized with nitrobenzene. Both pararosaniline and rosaniline are formed. (See 467, 468.) When these colorless bases are treated with hydrochloric acid they form colored salts by the elimination of water, as in the case of the formation of malachite green (465), thus: —



When parafuchsine (I) is treated with solutions of the alkalis it is first converted into an unstable, colored, substituted ammonium hydroxide (II) and this gradually goes over into the insoluble, colorless carbinol base, pararosaniline (III): —



Another method for the preparation of parafuchsine consists in the oxidation of diaminodiphenylmethane (463) and aniline in the presence of hydrochloric acid: —



The commercial fuchsine or magenta is a mixture of the colored (quinoid) chlorides of pararosaniline and rosaniline. It forms green crystals which dissolve in water with a red color. It dyes silk and wool directly a bluish red color, cotton only after mordanting with tannin and tartar emetic. Somewhat over 284,000 pounds of fuchsine or magenta were produced in the United States in 1920.



**Dyeing.** Silk and woolen fabrics can generally be dyed directly by placing them in a solution of a dye, cotton only in the case of certain substantive dyes (Congo red for example). Vegetable fabrics require as a rule previous treatment with a *mordant*. Aluminium, ferric and chromic hydroxides, obtained by saturating the fabric with the acetates of these metals and then steaming, are used as mordants with acid dyes, while tannin is employed with basic dyes.

**Acid fuchsine** is a mixture of the acid sodium salts of the di- and trisulphonic acids of rosaniline and pararosaniline, made by the action of fuming sulphuric acid on these bases and converting the sulphonic acids formed into the acid sodium salts. It is more soluble in water than fuchsine and is a valuable dye.

#### DERIVATIVES OF PARAROSANILINE AND ROSANILINE

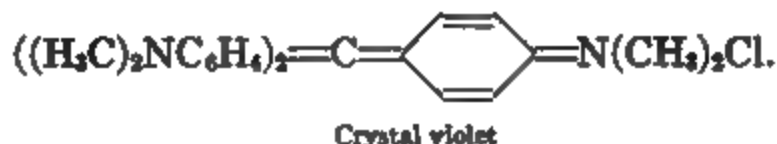
By the introduction of methyl or ethyl groups into fuchsine in the place of the amino hydrogens the red color of the dye is changed to violet, the intensity of the latter color depending on the number of alkyl groups introduced.

**Methyl violet** is made by oxidizing dimethylaniline with copper sulphate, phenol, and sodium chloride. The methane carbon atom necessary to combine the three phenyl residues is split off from part of the dimethylaniline. Consequently methyl violet is essentially a mixture of pentamethylparafuchsine and hexamethylparafuchsine. It dyes silk and wool a violet color, the shade being bluer the more methyl groups the dye contains. Over 600,000 pounds of methyl violet were produced in the United States in 1920.

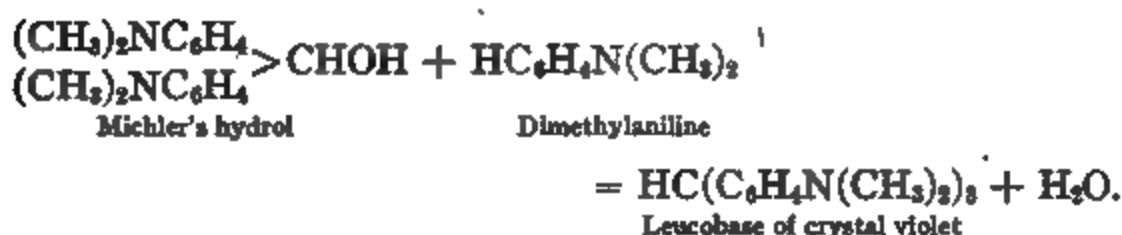
**Crystal violet** is hexamethylparafuchsine. It is one of the constituents of methyl violet and is characterized by its remarkable power of crystallization, whence the name. It is made by the action of dimethylaniline (1) on Michler's ketone (401) or (2) on Michler's hydrol (401): —



When the carbinol is treated with hydrochloric acid, water splits off, giving crystal violet,

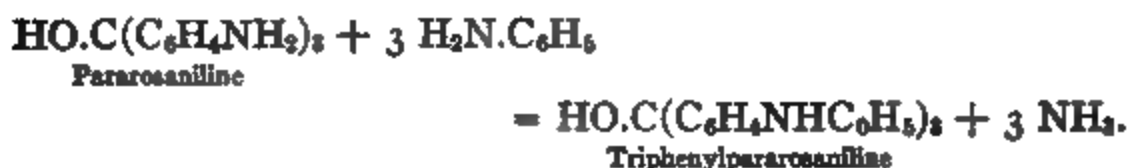


When Michler's hydrol is used the leuco base is first formed:—

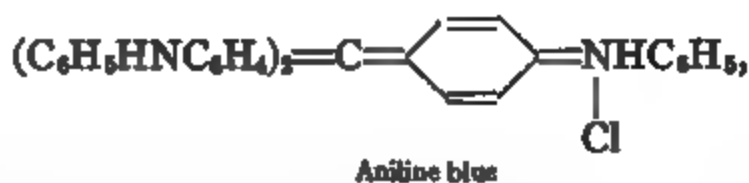


The leucobase is then oxidized to the dye base (carbinol) with lead peroxide as in the case of the preparation of malachite green (465), and the carbinol is combined with hydrochloric acid.

**Aniline blue.**—When pararosaniline or rosaniline is heated with aniline and benzoic acid, ammonia is eliminated and the triphenyl derivative is formed:—



As the anhydro-chloride of this base,

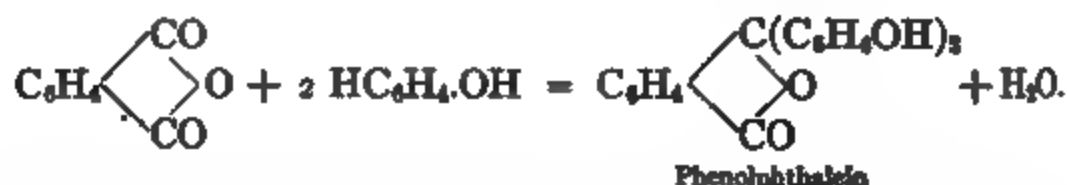


is insoluble in water, it has to be used in alcoholic solution. Triphenylpararosaniline is usually converted into sulphonic acids (mono-, di-, or trisulphonic acid) by the action of fuming sulphuric acid in order to render it soluble. The sodium salts of these acids are called *Soluble blue*, *Alkali blue*, *Cotton blue*, etc. About 783,000 pounds of Alkali blue and Soluble blue were produced in the United States in 1920.

## PHTHALEINS

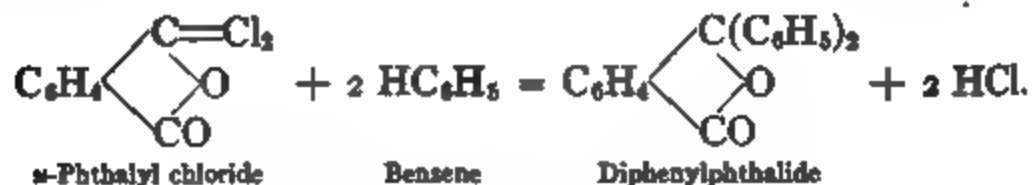
When a phenol is heated with phthalic anhydride and a dehydrating agent, water is eliminated and a *phthalein* is formed.

**Phenolphthalein**,  $C_{20}H_{14}O_4$ , is the simplest of all the phthaleins. It is formed by heating phenol and phthalic anhydride with concentrated sulphuric acid or with some other dehydrating agent: —



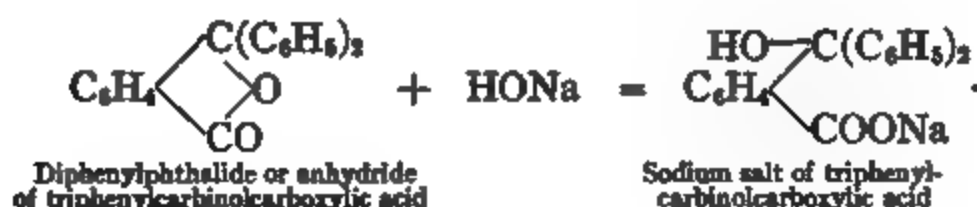
After the reaction is completed the mass is boiled with water to remove the sulphuric acid, unchanged phenol and phthalic anhydride, and the phenolphthalein dissolved in a solution of caustic soda. The solution is filtered to remove *fluoran* (476), the phenolphthalein precipitated by the addition of an acid and recrystallized from methyl alcohol. It crystallizes in the monoclinic system, is insoluble in water, and melts at  $250^\circ$ – $253^\circ$ . It dissolves in alkalis with a red color and is precipitated from this solution colorless by acids. It is used as an indicator in acidimetry and alkalimetry. It is made on the large scale and is used as a purgative. It is not a dye but is converted into a dye by introducing nitro groups. (Compare with phenol and picric acid.)

Phenolphthalein has been shown by Baeyer to be a derivative of triphenylmethane by means of the following reactions. When phthalic anhydride is treated with phosphorus pentachloride it gives phthalyl chloride (417), and this when heated with benzene in the presence of aluminium chloride gives diphenylphthalide:—

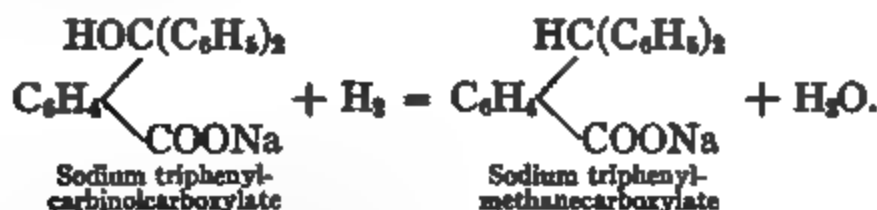


Diphenylphthalide when boiled with a concentrated solution

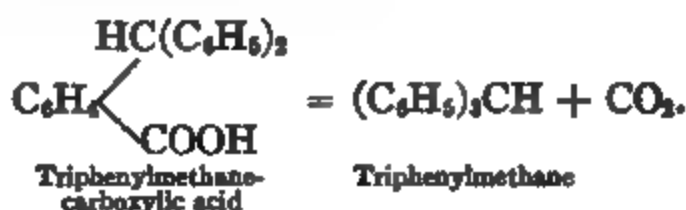
of caustic soda gives the sodium salt of triphenylcarbinolcarboxylic acid: —



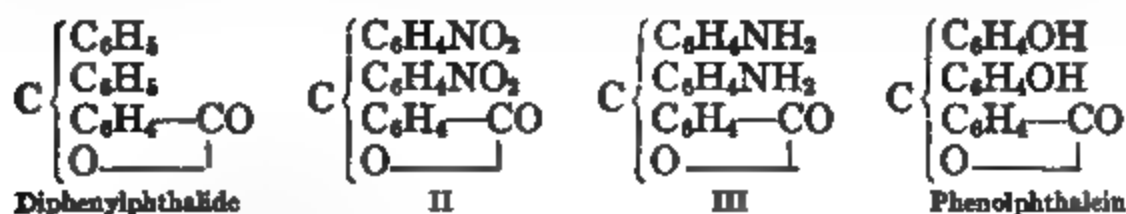
This sodium salt undergoes reduction to the sodium salt of triphenylmethanecarboxylic acid when its solution is boiled with zinc dust: —



The triphenylmethanecarboxylic acid, obtained from the sodium salt, by decomposing it with acids, gives triphenylmethane when heated with barium hydroxide: —

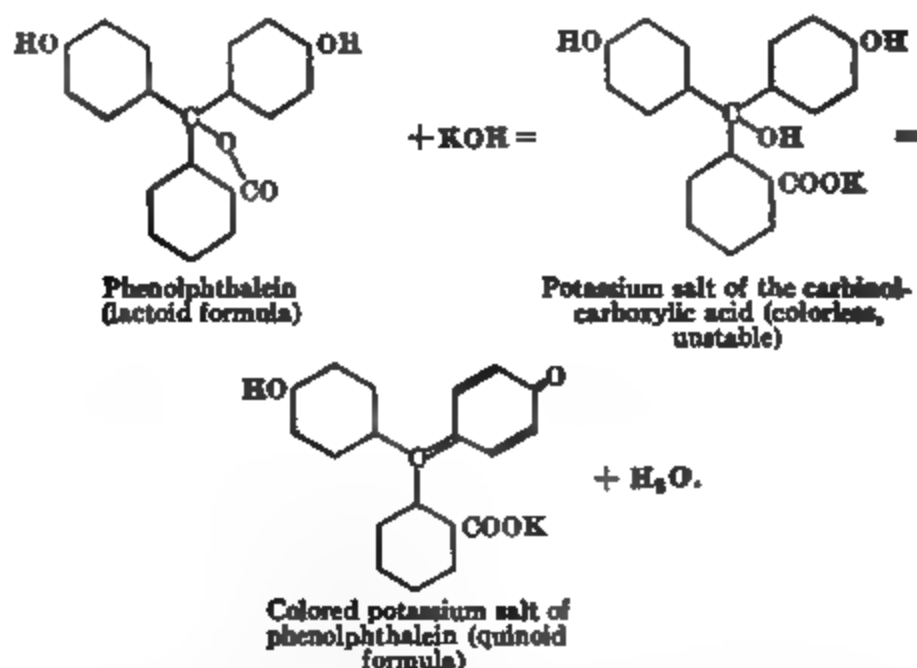


Having thus shown that diphenylphthalide is a derivative of triphenylmethane Baeyer then made phenolphthalein synthetically from it. On heating with nitric acid dinitrodiphenylphthalide (II) was made. This was then converted into diaminodiphenylphthalide (III) by reduction, and this when diazotized and boiled with water gave phenolphthalein: —



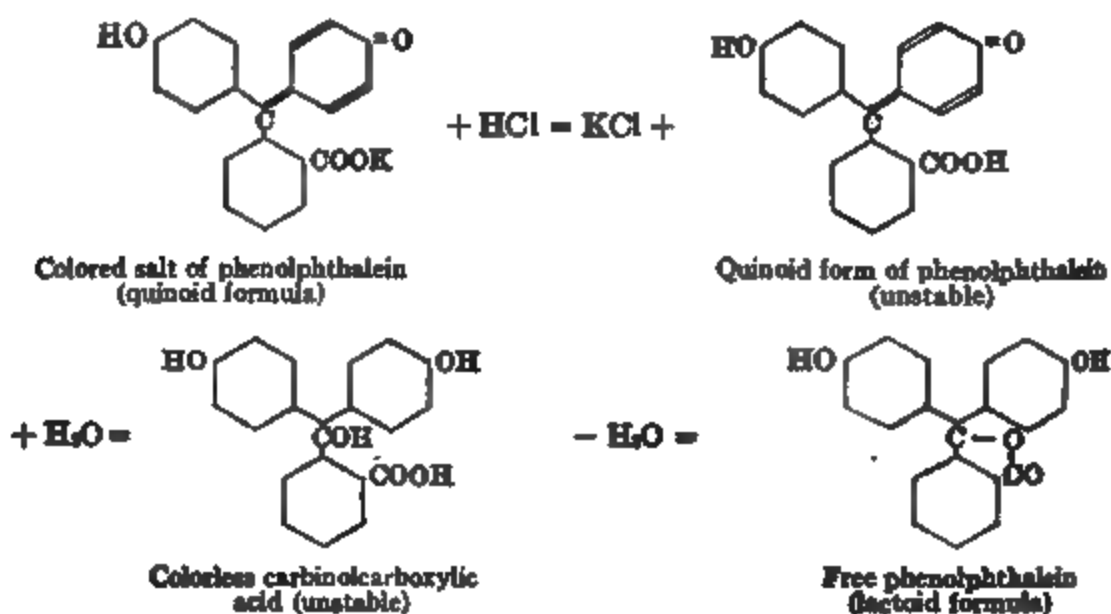
From this synthesis of phenolphthalein it will be seen that it is dihydroxydiphenylphthalide.

When phenolphthalein dissolves in solutions of the alkalis it gives a red color, due to the formation of the red sodium salt of the quinoid modification of phenolphthalein: —



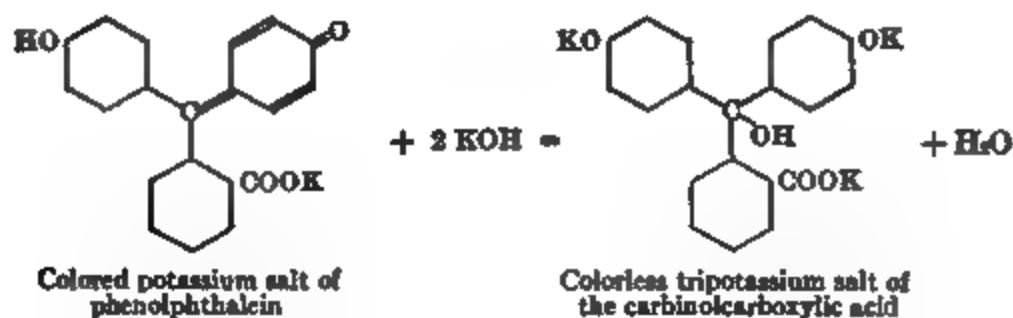
It will be noted that in alkaline solution water splits off to give the colored, quinoid salt, as in the case of the formation of parafuchsine from pararosaniline and hydrochloric acid (469).

When acid is added to the solution of this colored quinoid salt of phenolphthalein, the reverse changes take place, and phenolphthalein is precipitated: —

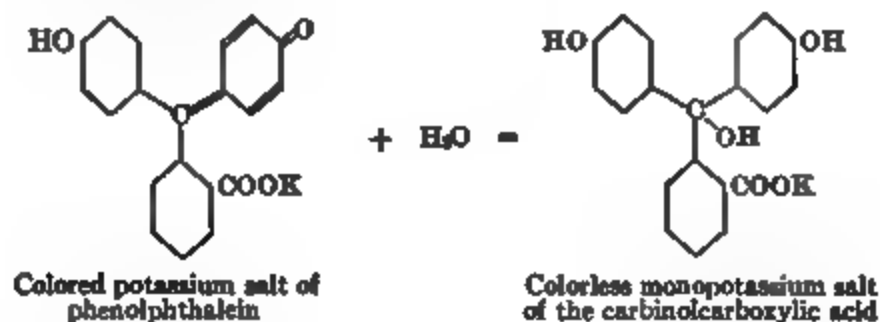


It will be noted that in acid solution water splits off to form the lactone ring.

When an excess of alkali is added to the colored solution of the potassium salt it becomes colorless. This is due to the formation of the tripotassium salt of the carbinolcarboxylic acid, which is colorless: —

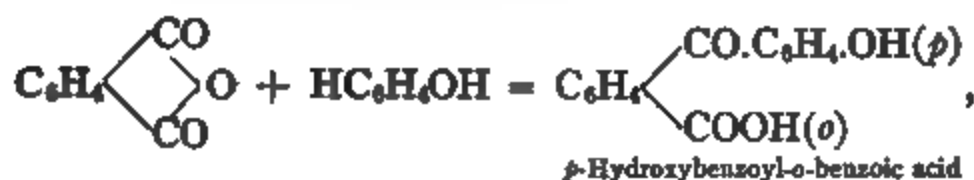


Alcohol also decolorizes the colored solution of the potassium salt of phenolphthalein in consequence of the formation of the salt of the carbinolcarboxylic acid: —

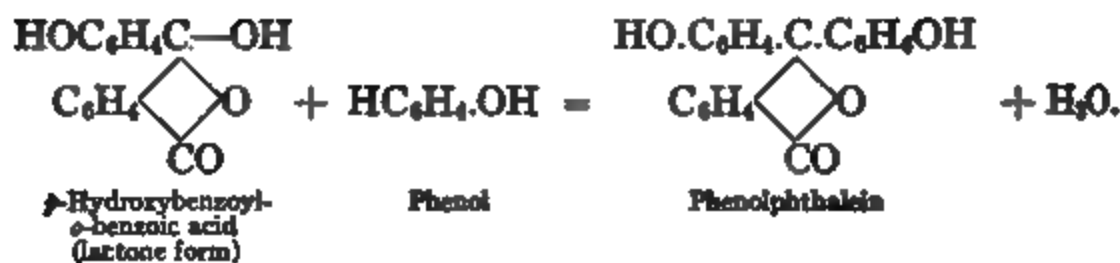


**NOTE FOR THE STUDENT.** — Note that all carbinols are colorless; color appears only when water splits off and the quinoid condition is established.

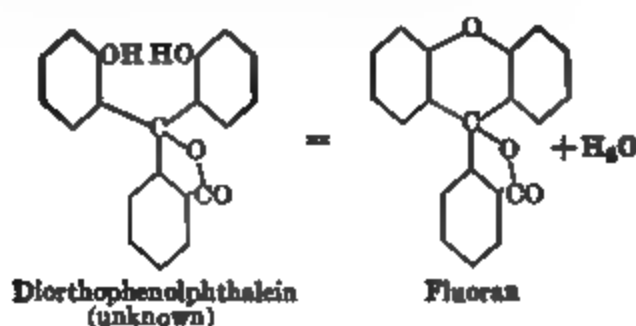
Recent investigations have shown that the formation of phenolphthalein and other phthaleins takes place in two stages: first the phthalic anhydride combines with a molecule of phenol to give *p*-hydroxybenzoyl-*o*-benzoic acid: —



and this then combines with another molecule of phenol to give phenolphthalein and water: —

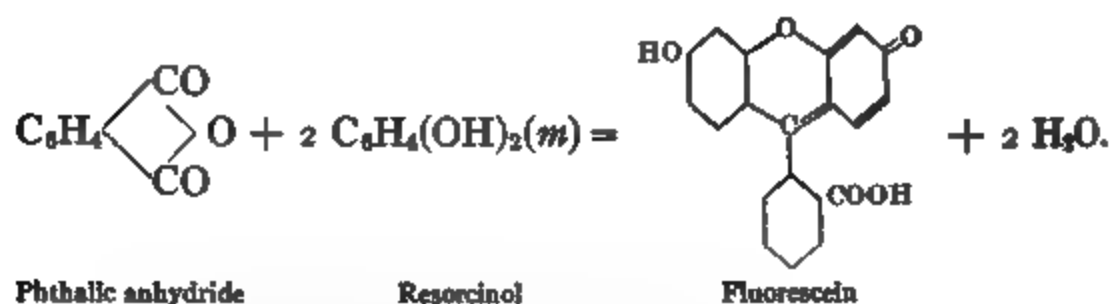


The formation of phenolphthalein, which is a dipara compound, is always accompanied by that of fluoran, which is removed from the phenolphthalein by dissolving it in solutions of the alkalis in which fluoran is insoluble. Fluoran has been shown to be the anhydride of diorthophenolphthalein: —



It is called fluoran as it is the mother substance of the fluorescein dyes.

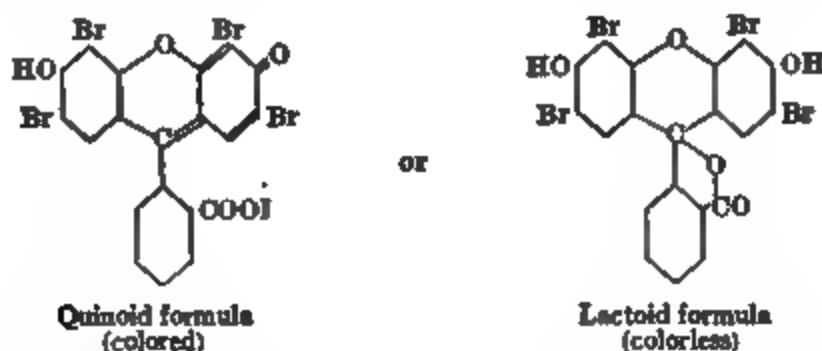
Fluorescein, anhydroresorcinolphthalein,  $\text{C}_{20}\text{H}_{12}\text{O}_5 + \text{H}_2\text{O}$ , is made on the large scale by heating resorcinol and phthalic anhydride with zinc chloride to  $200^\circ$ : —



The formation of fluorescein is analogous to that of phenolphthalein. The phthalic acid residue enters the two molecules of resorcinol in the para position to one of the hydroxyl groups and ortho to the other; and then the two hydroxyls in the ortho position lose a molecule of water as in the formation of fluoran. (See above.) The quinoid structure is given to fluorescein because it is a colored compound and contains a carboxyl

group. It dissolves readily in solutions of the alkalis or alkaline carbonates, and these solutions are wonderfully fluorescent (yellow by transmitted light and yellowish green by reflected light). The color of the solution is perceptible even when only one part of the salt is present in 16 million parts of water. The formation of fluorescein is therefore used as a test for resorcinol or phthalic acid. *Uranine* is the disodium salt of fluorescein. Fluorescein dyes silk and wool yellow, but is not used as a dye. Its halogen derivatives, however, are important dyes.

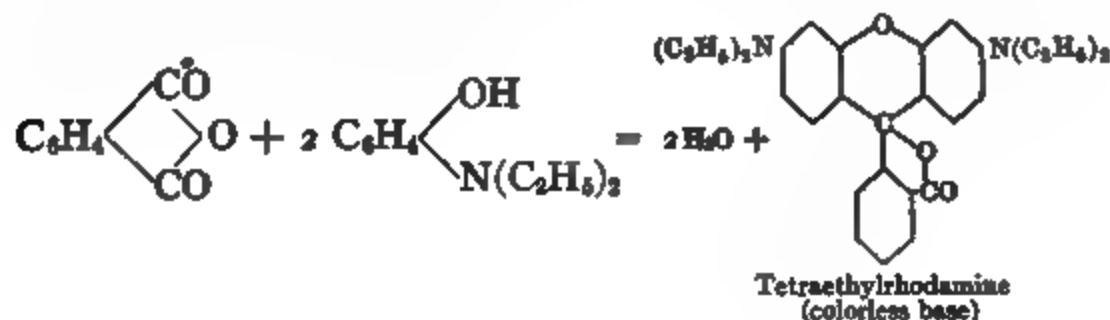
**Eosin** is tetrabromofluorescein made by brominating fluorescein: —



It crystallizes from aqueous alcohol in flesh-colored crystals, which may be a mixture of the colorless, lactoid form, and of the colored, quinoid form. The alcoholic solution is reddish yellow. On the addition of even a trace of alkali a yellowish-green fluorescence makes its appearance. The colored disodium or dipotassium salt forms the *soluble eosin* of commerce. Eosin is used in dyeing wool, silk and cotton. Nearly 86,000 pounds were made in the United States in 1920.

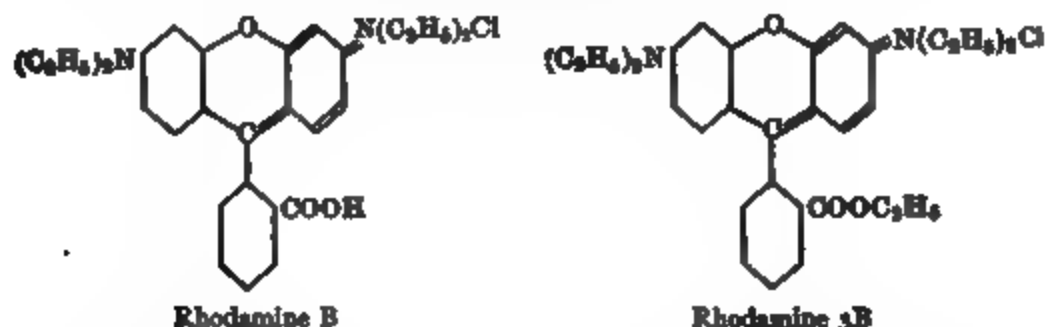
The *Rhodamine dyes* are closely related to fluorescein.

**Tetraethylrhodamine** is formed by fusing phthalic anhydride and diethyl-*m*-aminophenol with a condensing agent: —





The base itself is colorless and therefore has the lactoid formula as given above. When it is dissolved in hydrochloric acid it gives the colored tetraethylrhodamine hydrochloride : —

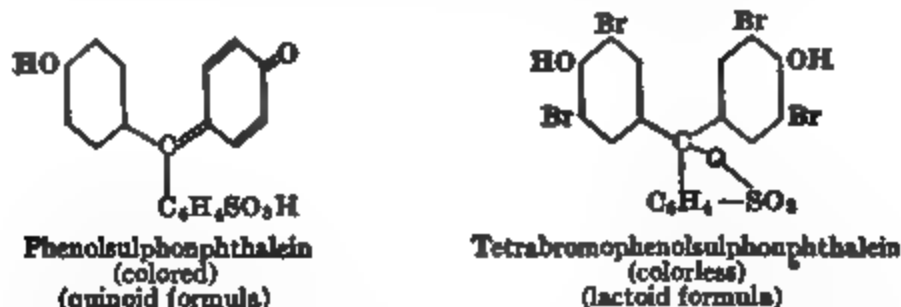


This forms green crystals which dissolve in water and alcohol with a bluish red color. It dyes silk a magnificent red with an intense greenish yellow fluorescence. Rhodamine 3B is the ethyl ester of rhodamine B. It is formed by esterifying rhodamine B by heating it with alcoholic hydrochloric acid. This reaction shows the presence of the free carboxyl group in rhodamine B.

#### SULPHONPHTHALEINS

These compounds are completely analogous to the phthaleins. They are formed by heating the phenols with the anhydride of *o*-sulphobenzoic acid (412) or with the chlorides of that acid.

Phenolsulphonphthalein is a bright red crystalline powder somewhat soluble in water, more so in alcohol. From the fact that it is a colored compound, while its tetrabromo derivative is colorless, they are given the following formulas : —

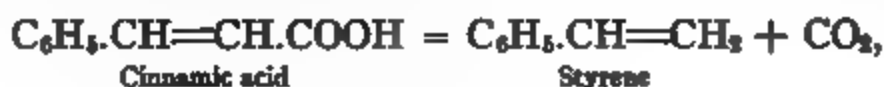


Phenolsulphonphthalein is used in medicine as a functional test for the kidneys and in diagnosing diseases of the kidneys. For the names *phenol red* and *bromophenol blue* it and its bromo derivative are used as indicators.

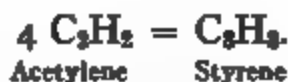
## CHAPTER XVII

### PHENYLETHYLENE AND DERIVATIVES

**Styrene, phenylethylene,  $C_6H_5.CH=CH_2$ .**—This hydrocarbon is found in the resin, liquid storax, and in coal tar. It is formed when cinnamic acid (479) is heated to its boiling point:—



and by the polymerization of acetylene:—

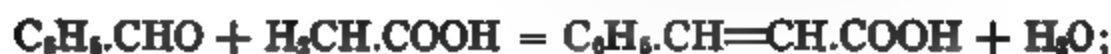


It is a liquid with a pleasant odor, boiling at  $145.5^\circ$ – $146^\circ$ , insoluble in water but miscible with alcohol and ether in all proportions. When heated or even when allowed to stand it undergoes polymerization to the solid, *metastyrene*. Styrene like ethylene (277) combines with chlorine and bromine, forming a dichloride,  $C_6H_5.CHCl.CH_2Cl$ , and a dibromide,  $C_6H_5.CHBr.CH_2Br$ . With hydrobromic acid it forms phenylethylbromide,  $C_6H_5.CHBr.CH_3$ . Chromic acid converts it into benzoic acid (322). Homologues of styrene, such as phenylpropylene, phenylbutylene, etc., have been prepared.

**Cinnamyl alcohol, styryl alcohol,  $C_6H_5.CH:CH.CH_2OH$ ,** occurs in the form of the ethereal salt of cinnamic acid in liquid storax, and also in the balsam of Peru. It crystallizes in needles that melt at  $33^\circ$ . It is somewhat soluble in water, has an odor of hyacinths, and boils at  $254^\circ$ – $255^\circ$ . When oxidized with platinum black it gives *cinnamic aldehyde*,  $C_6H_5.CH=CH.CHO$ , the chief constituent of the oil of cinnamon; and by further oxidation cinnamic acid.

**Cinnamic acid, phenylacrylic acid,  $C_6H_5.CH=CH.CO_2H$ ,** occurs partly free and partly in combination in the form of esters in many balsams and resins (storax, balsams of Peru and Tolu,

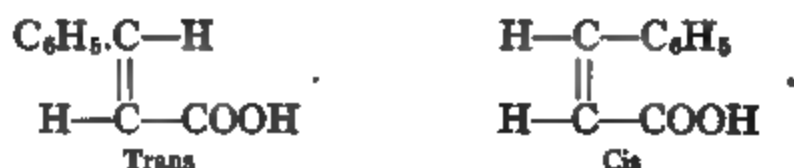
etc.). It can be made by heating benzaldehyde with sodium acetate and acetic anhydride (Perkin's synthesis (397)) : —



or by treating benzal chloride with sodium acetate : —



It crystallizes from hot water in monoclinic prisms which melt at  $134^\circ$ . When rapidly distilled it boils at  $300^\circ$ , but when distilled slowly it decomposes into styrene and carbon dioxide. Oxidizing agents convert it first into benzaldehyde, and then into benzoic acid. It combines with nascent hydrogen to form hydrocinnamic or phenylpropionic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}$  (415), and with bromine to form cinnamic acid dibromide,  $\text{C}_6\text{H}_5\text{CHBr.CHBr.COOH}$ . The ordinary cinnamic acid is the trans-form : —



It is converted into the cis-form by the action of ultraviolet light.

When nitrated cinnamic acid gives ortho- and paranitrocinnamic acids, which are converted into the corresponding amino cinnamic acids by reduction. The orthoaminocinnamic acid,



and forms the anhydride, *carbostyryl* ( $\alpha$ -hydroxyquinoline) : —

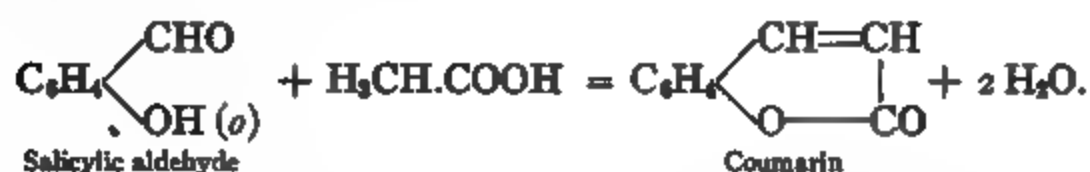


Carbostyryl is a tautomeric substance. In the free state it probably has the lactam structure, while the sodium salt is

derived from its tautomeric form,  $\alpha$ -hydroxyquinoline (509) which acts like a phenol.

Coumarin,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{O} \text{---} \text{CO} \end{array}$ , is the anhydride of the cis form

of orthohydroxycinnamic acid. It is found in tonka beans and is the odoriferous principle of woodruff (*Asperula odorata*). It is also found in dates, in Peru balsam, and is very widely distributed in nature. Synthetically it was first obtained by Perkin from salicylic aldehyde, sodium acetate, and acetic anhydride:—



It crystallizes in rhombic prisms, has a pleasant spicy odor, and a bitter taste. In very great dilution it has the odor of *new-mown hay*. It melts at  $69^\circ\text{--}70^\circ$ , is difficultly soluble in water, readily in alcohol and ether. When boiled with a solution of concentrated caustic potash it is hydrolyzed to a salt of orthocoumaric acid, which is stereoisomeric with coumarinic acid:—

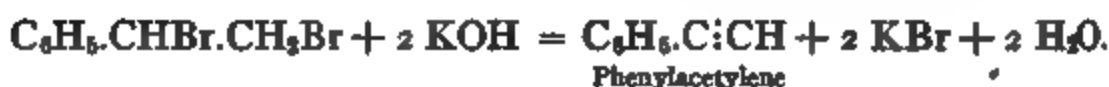
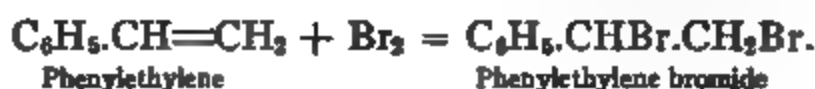


Coumarinic acid itself is not known. As soon as it is set free from its salts it forms the anhydride, coumarin. *o*-Coumaric acid is converted into coumarin by the action of acetic anhydride. Coumarin is made on the large scale from *o*-cresol, and is used in perfumery and in the preparation of flavoring extracts.

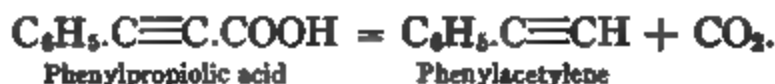
## CHAPTER XVIII

### PHENYLACETYLENE AND DERIVATIVES

Phenylacetylene,  $C_6H_5.C\equiv CH$ , can be made from styrene in the same way that acetylene is made from ethylene:—



It is most readily obtained by the distillation of phenylpropionic acid:—



It is a liquid boiling at  $142^\circ$ . Like acetylene it gives a silver compound,  $C_6H_5.C\equiv CAg$ , and combines with four atoms of bromine.

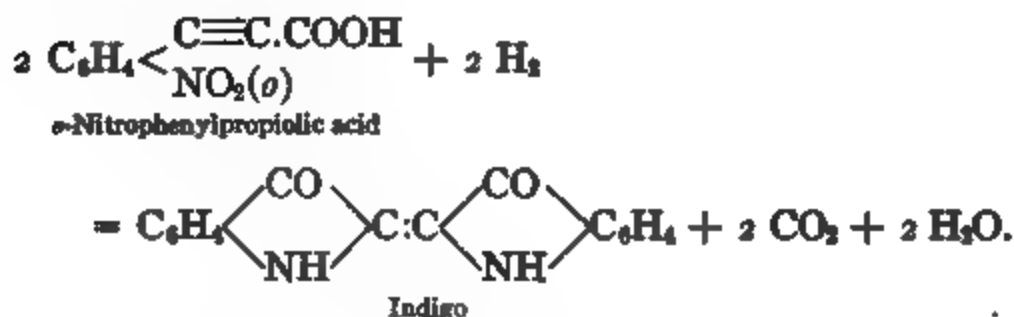
Phenylpropionic acid,  $C_6H_5.C\equiv C.COOH$ , is made from cinnamic acid in the same way that phenylacetylene is made from styrene:—



It crystallizes in needles that melt at  $136^\circ$ – $137^\circ$ . When heated it loses carbon dioxide and forms phenylacetylene.

Orthonitrophenylpropionic acid,  $O_2N.C_6H_4.C\equiv C.COOH$ , is made from orthonitrocinnamic acid in the same way that phenylpropionic acid is made from cinnamic acid. It crystallizes in colorless needles which decompose at  $155^\circ$ – $156^\circ$ . When heated with water it loses carbon dioxide and gives *o*-nitrophenylacetylene. It is of special interest because of the ease

with which it can be converted into indigo. When heated in alkaline solution in the presence of a mild reducing agent, such as glucose, it yields indigo:—



### INDIGO AND RELATED COMPOUNDS

Indigo is the oldest and most valuable dye known. Mummy cloth which is at least 4000 years old has been shown to be dyed with it. Eighteen million pounds (20 per cent paste), valued at about \$13,500,000, were produced in the United States in 1920. Until recently all the indigo was obtained from the indigo plants (such as *Indigofera sumatrana* and *I. arrecta*) which were grown on the large scale in India, Java, China, Japan, and in South America, but most of that now used is made synthetically from benzene. Indigo is present in the plant in the form of a glucoside, *indican*,  $\text{C}_{14}\text{H}_{17}\text{NO}_6 + 3 \text{ H}_2\text{O}$ , which occurs chiefly in the leaves. The plant also contains an enzyme, which in the presence of water hydrolyzes the indican

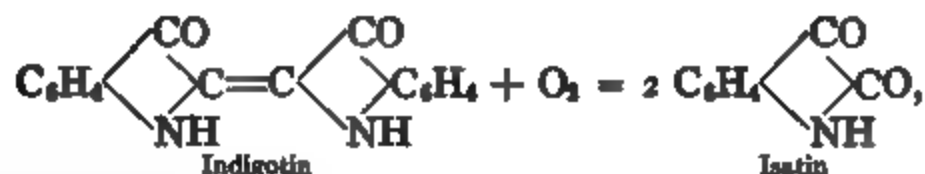
to glucose and *indoxyl*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}=\text{CH} \\ \text{C}-\text{OH} \end{array}$ , and the indoxyl is then

oxidized to indigo by the air, lime being added to render the solution alkaline. (See below.) The natural indigo of commerce contains indigluclin, indigo brown, indirubin, and other impurities in addition to the blue dye *indigotin*. The synthetic dye is practically pure indigotin.

Indigo blue, indigotin,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ , is a dark blue powder which when rubbed takes on a coppery luster. It sublimes in copper-red prisms and is insoluble in most solvents. It can be crystallized from hot aniline or nitrobenzene. It does not dis-

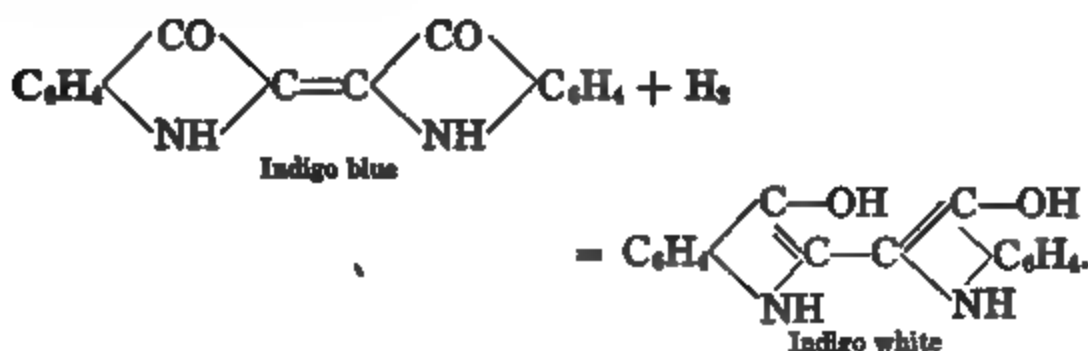


This formula not only explains the ease with which indigotin is oxidized to isatin :—

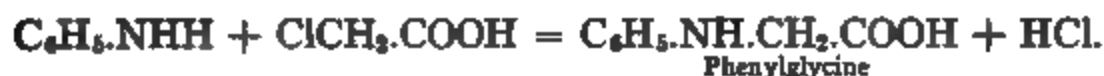


and the fact that it is formed practically quantitatively by the oxidation of indoxyl (see below), but is in accord with its entire chemical conduct.

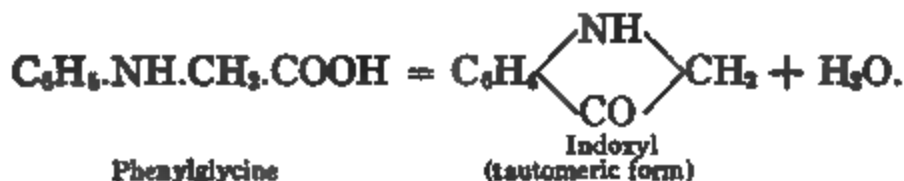
*Indigo white*, as stated above, is the product of reduction of indigo blue :—



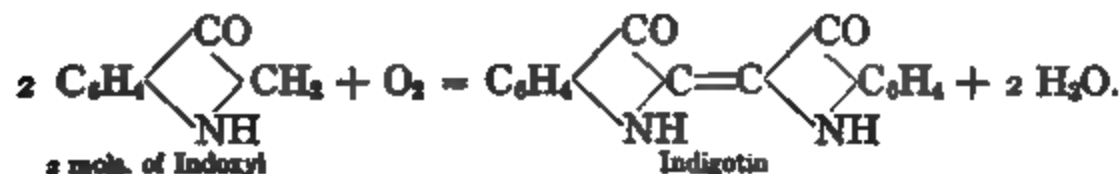
**Synthetic indigo** is now manufactured on the large scale from aniline. There are three methods which are of importance. In the first of these aniline is condensed with monochloroacetic acid to form phenylglycine :—



Phenylglycine is then heated with sodium amide, when indoxyl is formed by the elimination of water :—



The indoxyl is then oxidized in alkaline solution by air to indigotin :—





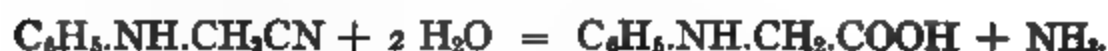
The second process differs from the first only in the method used to convert aniline into phenylglycine. From that point on the methods are the same. In this method aniline is condensed in aqueous solution with the sodium bisulphite compound of formaldehyde:—



The resulting product, which is sodium  $\omega$ -methylanilinesulphonate, reacts in aqueous solution with sodium cyanide to give the nitrile of phenylglycine:—

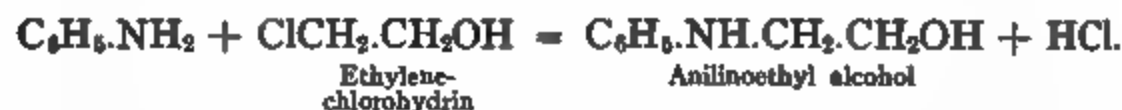


and this on hydrolysis gives phenylglycine:—

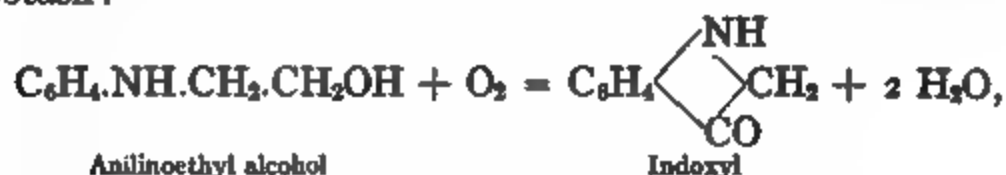


All these reactions take place practically quantitatively in aqueous solutions, and only the phenylglycine is isolated.

The third method depends upon the fact that aniline combines with ethylene chlorohydrin (152) to form anilinoethyl alcohol (349):—



This product is converted into indoxyl by fusion with caustic potash:—



and the indoxyl is oxidized to indigotin in the usual manner.

When indigo is sulphonated it gives a disulphonic acid in which the two sulphonic acid groups are in the para positions to the imino groups. The disodium salt of this acid, which is readily soluble in water, is the *indigo carmine* of commerce formerly much used in dyeing wool and silk. It is now used in the manufacture of writing inks. The bromoindigos made by the direct bromination of indigo are very important and valuable vat dyes. The dibromoindigo, made synthetically, in which the two

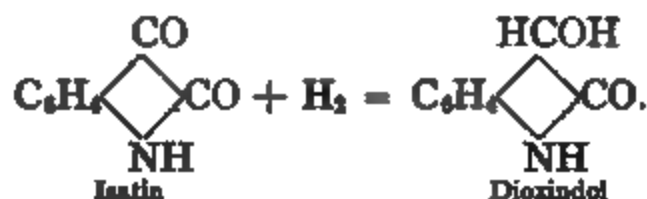
bromine atoms are in the para positions to the carbonyl groups has been found to be identical with the purple of antiquity (Tyrian purple). It was obtained by the Phoenicians from the mollusc, *Murex brandaris*.

A number of compounds closely related to indigo were obtained by Baeyer in the course of his investigation of the

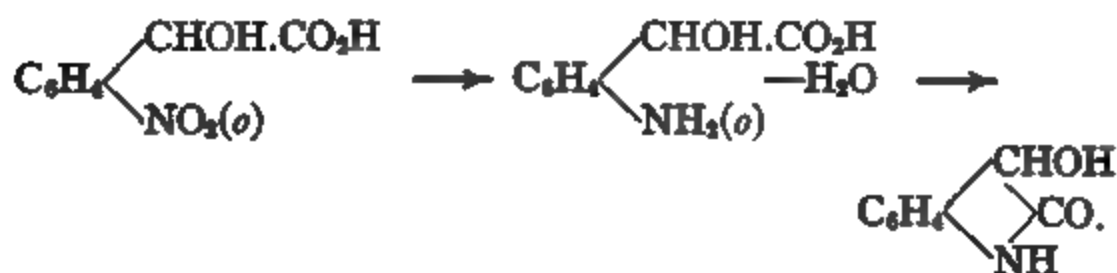
reduction products of isatin,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{NH} \end{array} \text{CO}$  (409).

Dioxindol,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{HCOH} \\ \diagdown \text{NH} \end{array} \text{CO}$ , which is the anhydride of ortho-aminophenylglycolic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CHOH.COOH} \\ \diagdown \text{NH}_2(o) \end{array}$ , is formed by

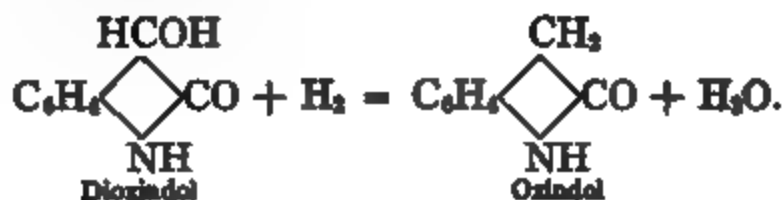
reducing isatin with zinc dust and hydrochloric acid: —



It is formed also by the reduction of *o*-nitrophenylglycolic acid with zinc dust in acetic acid solution: —



It yields isatin on oxidation and can also be obtained by the oxidation of oxindol. It crystallizes in colorless prisms which melt at 167°–168° and are readily soluble in water, alcohol, and ether. On reduction with sodium amalgam in mineral acid solution it gives oxindol (414): —



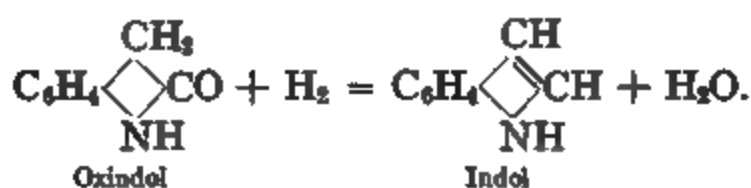
Indoxyl,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{COH} \\ \diagdown \text{CH} \\ \text{NH} \end{array}$ , isomeric with oxindol, results from the

fusion of indigo with caustic potash, and is the intermediate product in the formation of indigo, both the *natural* and the *synthetic*. It acts as a tautomeric substance and yields deriv-

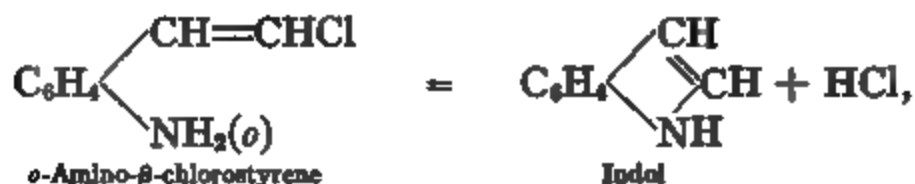
atives of the pseudo form,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CH}_2 \\ \text{NH} \end{array}$ . It occurs in yellow

crystals melting at  $85^\circ$ , is soluble in hot water, with a yellow-green fluorescence, and is volatile with superheated steam. It dissolves in concentrated hydrochloric acid, with a red color. It is an extremely unstable substance and resinifies very readily. It is oxidized almost quantitatively in alkaline solution by the air to indigo. It forms a nitroso compound and hence contains an imino group. On heating with potassium pyrosulphate,  $\text{K}_2\text{S}_2\text{O}_7$ , it forms potassium indoxyl sulphate,  $\text{C}_6\text{H}_4\text{NOSO}_2\text{K}$ , a constituent of the urine (urine indican). This reaction shows the presence of the hydroxyl group.

Indol,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH} \\ \diagdown \text{CH} \\ \text{NH} \end{array}$ , was first obtained by distilling oxindol with zinc dust: —



It is also formed from *o*-amino- $\beta$ -chlorostyrene by the elimination of hydrochloric acid: —



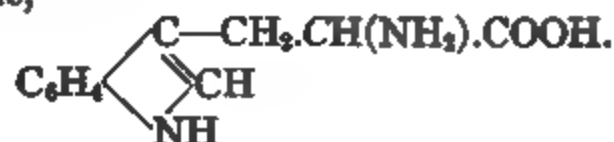
and this synthesis establishes the structure of the substance. It is present in coal tar in small quantity and may be isolated

from the fraction boiling between  $240^{\circ}$  and  $260^{\circ}$ . It is also present in the oil of jasmine and in neroli oil. It crystallizes in white leaflets which melt at  $52.5^{\circ}$ , and is volatile with steam. The impure product has a very disagreeable fecal odor. The pure substance, however, has a pleasant floral odor and is used in perfumery. It forms indigo when oxidized with ozone.



has been found in civet, and, with indol, in the wood of the tree *Celtis reticulosa*. It also occurs in human feces and is the cause of its disagreeable odor. It is formed together with indol in the putrefaction of the proteins and also by fusing the proteins with caustic soda. It crystallizes in colorless leaflets which melt at  $95^{\circ}$ , and when impure it has a strong odor of feces. Like indol, skatol is made artificially and is used in the manufacture of floral perfumes.

**Tryptophan**, a product of the hydrolysis of the proteins, is  $\beta$ -indolalanine,



It has also been made synthetically. The synthetic product is optically inactive; the tryptophan from the proteins is levorotatory.

**NOTE FOR STUDENT.** — Does it contain an asymmetric carbon atom?

## CHAPTER XIX

### HYDROCARBONS CONTAINING TWO BENZENE RESIDUES IN DIRECT COMBINATION

Just as the marsh gas residue, methyl,  $\text{CH}_3$ , unites with methyl to form ethane,  $\text{H}_3\text{C}.\text{CH}_3$ , so the benzene residue, phenyl,  $\text{C}_6\text{H}_5$ , unites with phenyl to form the hydrocarbon diphenyl,  $\text{H}_5\text{C}_6.\text{C}_6\text{H}_5$ , and residues of toluene and of the higher members of the series unite in a similar way to form homologues of diphenyl.

**Diphenyl,  $\text{C}_{12}\text{H}_{10}$ ,  $(\text{C}_6\text{H}_5.\text{C}_6\text{H}_5)$ .**—This hydrocarbon is made by treating bromobenzene with sodium:—



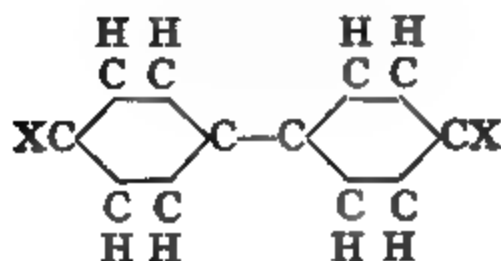
and by conducting benzene through a tube heated to redness:—



It forms large, lustrous plates. It melts at  $70.5^\circ$ , and boils at  $254^\circ$ . It is easily soluble in hot alcohol and ether.

Diphenyl is an extremely stable substance. It resists the action of ordinary oxidizing agents, but with strong ones it yields benzoic acid. A large number of derivatives of diphenyl have been studied.

*Substitution products of diphenyl.*—Substituting agents, as the halogens, nitric and sulphuric acids, act upon diphenyl much in the same way as they do upon toluene. Of the mono-substitution products, three varieties, ortho, meta, and para, are possible. Of these the para derivatives are most easily obtained by direct action. At the same time ortho derivatives are formed to some extent. By further action ortho-para products and di-para products are formed. In the latter the substituting atoms or groups occupy the positions indicated on the next page:—



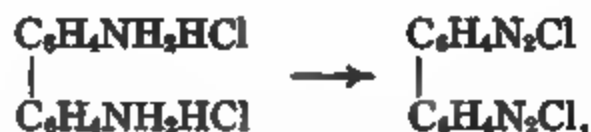
Benzidine,  $\begin{array}{c} \text{C}_6\text{H}_4\text{NH}_2(p) \\ | \\ \text{C}_6\text{H}_4\text{NH}_2(p) \end{array}$ . — This is diparadiaminodiphenyl.

It is formed by the reduction of diparadinitrodiphenyl, and also from hydrazobenzene (360) made by the reduction of nitrobenzene in alkaline solution. When this is treated with mineral acids it is transformed into benzidine:—



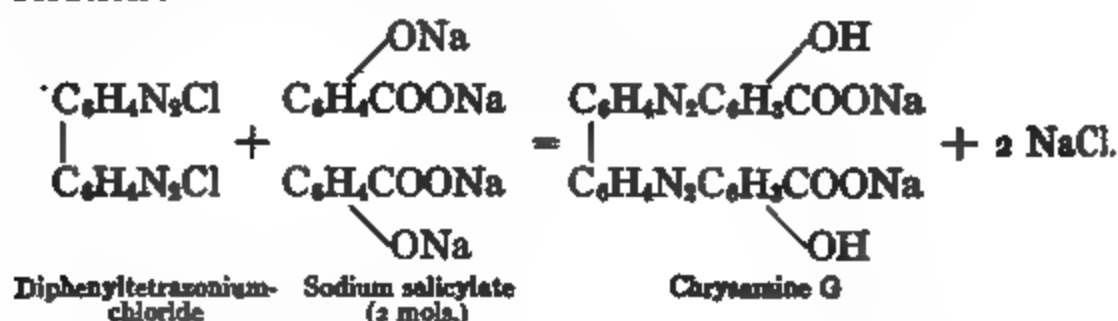
Benzidine is manufactured on the large scale by this method. It crystallizes from hot water in leaflets that melt at  $127.5^\circ$ – $128^\circ$ . It is difficultly soluble in water, more readily in alcohol and ether. It boils at  $400^\circ$ – $401^\circ$ . The sulphate,  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{H}_2\text{SO}_4$ , and the chromate,  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{H}_2\text{CrO}_4$ , both difficultly soluble in water and alcohol, are characteristic salts. The sulphate crystallizes in scales and is used to estimate benzidine or sulphuric acid quantitatively. The chromate has a deep blue color and crystallizes in needles. Over 2,000,000 pounds of benzidine were made in the United States in 1920.

**Benzidine dyes.** — Benzidine and its homologues (*o*-tolidine,  $\text{C}_{12}\text{H}_9(\text{CH}_3)_2(\text{NH}_2)_2$ , made from *o*-nitrotoluene, etc.) are of great importance in the manufacture of azo dyes. When the dihydrochloride is diazotized with nitrous acid it gives diphenyltetrazonium chloride:—



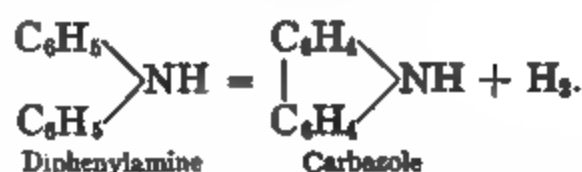
and this reacts readily with phenol acids, naphthylamine-

sulphonic acids (505) and naphthol sulphonic acids (502) to form valuable disazo dyes that dye cotton directly without the use of a mordant. They are therefore called *direct* or *substantive* dyes. The first dye of this class was called *Congo red* (506). *Chrysamine G*, an important disazo dye, is made by the action of diphenyltetrazonium chloride on sodium salicylate in alkaline solution:—



Carbazole,  $\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{NH}$ , the imide of diphenyl, is found in coal

tar and is obtained from the anthracene fraction by distilling it with sodium and potassium hydroxides. The carbazole forms a non-volatile potassium or sodium salt with the fused alkalis, in which the hydrogen of the imide group is replaced by the metal, while anthracene and the other hydrocarbons distil. The alkali salt of carbazole is then decomposed by water, the carbazole and alkali recovered, and the carbazole purified by sublimation. It is formed by passing the vapor of *o*-aminodiphenyl over red hot lime or the vapor of diphenylamine through a red hot tube (compare with the formation of diphenyl from benzene):—

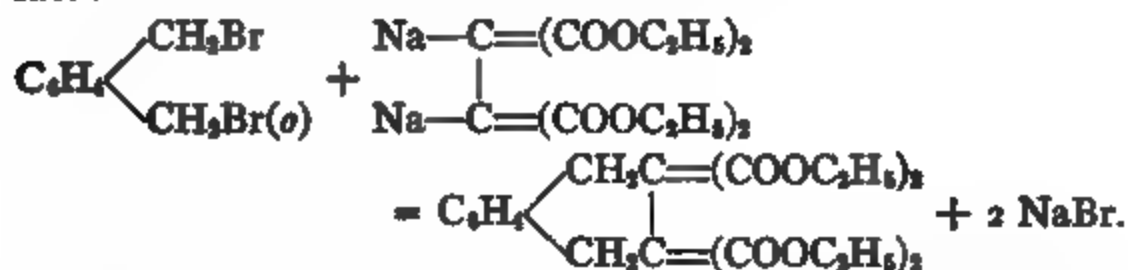


It crystallizes in colorless leaflets that melt at  $238^\circ$  and are sparingly soluble in alcohol, ether, and benzene. It distils at  $338^\circ$ , sublimes readily, and is exceedingly stable. It yields an acetyl and a nitroso compound, and a potassium salt,  $(\text{C}_6\text{H}_4)_2\text{NK}$ , when fused with caustic potash, showing the presence of the

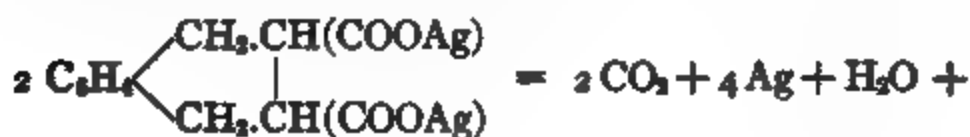
imide group. It is used in the manufacture of *Hydron blue*, a valuable vat dye.

**Naphthalene,  $C_{10}H_8$ .** — This hydrocarbon is the constituent of coal tar which is present in largest amount, about 6–15 per cent of the tar being naphthalene.<sup>1</sup> It crystallizes out of the fractions boiling between  $110^{\circ}$ – $270^{\circ}$ , and after it is freed from oil by centrifuging and pressure, is purified by washing it with small amounts of sulphuric acid and distilling in steam or subliming it. Large quantities of naphthalene are now obtained from the gases of the coking ovens. Naphthalene is also formed when marsh gas, ethylene, acetylene, or the vapors of alcohol, ether, acetic acid, benzene, toluene, etc., are passed through a red-hot tube. It crystallizes in colorless, monoclinic plates that melt at  $80^{\circ}$  and are insoluble in water, but dissolve readily in hot alcohol and benzene. It boils at  $218^{\circ}$ , is volatile with steam and sublimates very readily. It has a characteristic tarry odor. It gives phthalic anhydride (416) on oxidation, which shows that it is an ortho derivative of benzene. Its structural formula is based on the following syntheses from benzene derivatives:—

1. When *o*-xylylene dibromide is heated with the disodium compound of the ethyl ester of symmetrical ethanetetracarboxylic acid it forms ethyl tetrahydronaphthalenetetracarboxylate:—

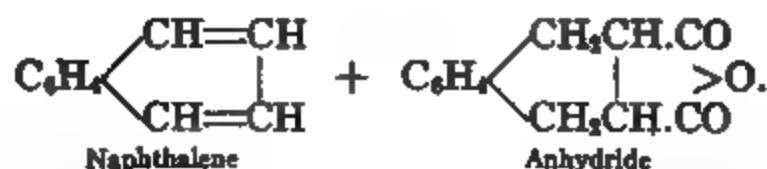


When this ester is saponified it loses two molecules of carbon dioxide (160), forming tetrahydronaphthalenedicarboxylic acid, and the silver salt of this acid when heated gives naphthalene and the anhydride of the acid:—



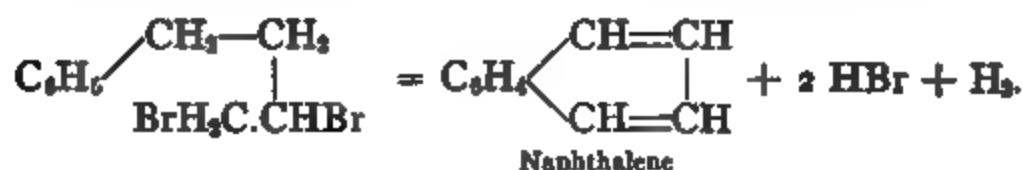
<sup>1</sup> See Lunge's *Coal Tar and Ammonia*, Fifth ed. 1916.



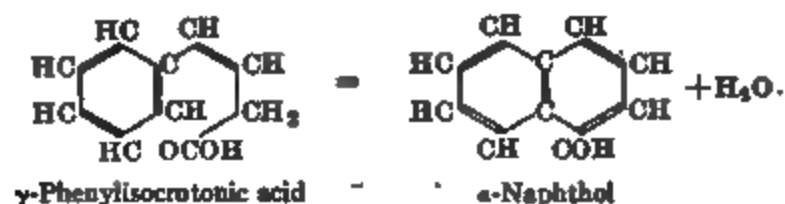


The anhydride of the acid also yields naphthalene when its vapor is passed through a red-hot tube. (Write the equation.)

2. Phenylbutylene dibromide gives naphthalene when its vapor is passed over lime heated to a red heat:—



3.  $\gamma$ -Phenylisocrotonic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}=\text{CHCH}_2\cdot\text{COOH}$ , loses water when heated and is converted into  $\alpha$ -naphthol, a hydroxyl derivative of naphthalene:—



When heated with zinc dust  $\alpha$ -naphthol gives naphthalene.

According to these syntheses naphthalene is made up of two benzene residues having two ortho carbon atoms in common, and this formula is in accord with the entire chemical conduct of the substance. It resembles benzene very closely, *e.g.*, it forms nitro compounds with nitric acid and sulphonic acids with sulphuric acid, the nitro compounds undergo reduction to amino derivatives of naphthalene and these can be diazotized in exactly the same way that aniline is. The sulphonic acids are converted into hydroxynaphthalenes by fusing with alkalis, and these substances (called naphthols) resemble the phenols closely.

The presence of two benzene rings in naphthalene has also been shown in the following manner: Nitronaphthalene, obtained by the direct action of nitric acid on naphthalene, yields nitrophthalic acid on oxidation with chromic acid:—

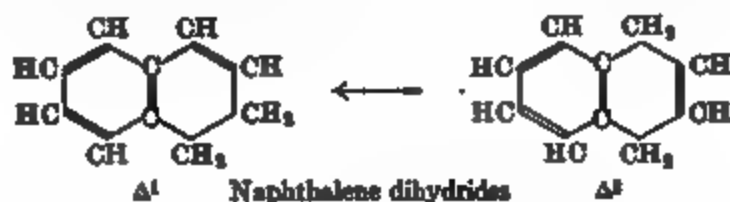


which can also be prepared by the direct nitration of phthalic acid. Hence the ring into which the nitro group has entered is a benzene ring. If, however, nitronaphthalene is reduced to aminonaphthalene and this is oxidized with potassium permanganate, phthalic acid is formed:—



It follows, therefore, that the second ring in naphthalene is also a benzene ring. Further, it has been shown that naphthalene-sulphonic acid yields both sulphophthalic acid and phthalic acid on oxidation.

The hydrogen addition products of naphthalene are also in accord with the above formula. When treated with metallic sodium in alcoholic solution naphthalene takes up two atoms of hydrogen to form dihydronaphthalene,  $C_{10}H_{10}$ , and this compound like dihydrobenzene (329) acts like an unsaturated compound, taking up bromine with great ease. In addition to this dihydride, which is called  $\Delta^2$  to indicate the position of the double bond, a second dihydride  $\Delta^1$  has been made by heating  $\Delta^2$  with sodium ethylate. It is also characterized by the ease with which it combines with bromine. These two dihydrides are exactly analogous to the two dihydrobenzenes and are the only ones possible according to the theory:—



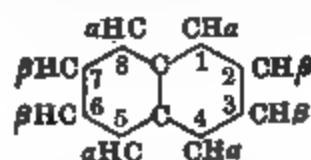
On further reduction naphthalene forms a tetrahydride,  $C_{10}H_{12}$ , and the final product is a decahydride,  $C_{10}H_{18}$ , which acts like a saturated hydrocarbon of the paraffin series:—



Naphthalene tetrahydride and decahydride are now made on the large scale by reducing naphthalene with hydrogen in the presence of nickel as a catalyst. They are both liquids, and are used as fuel in gas engines in place of gasolene. They are known in the trade as *tetralin* and *decalin*.

Over 37 million pounds of naphthalene were produced in the United States in 1920, almost one-third of which was from the gases of the coking ovens. The most important uses of naphthalene are in making derivatives, which are used in very large quantities in the manufacture of azo dyes; and for the preparation of phthalic anhydride, which is used in making the phthalein dyes, anthraquinone, and phenolphthalein. Large quantities are used in the manufacture of lampblack and for heating purposes. It is used in preserving wood, hides, and furs, and as a fuel in motors. It is also used as an antiseptic and an insecticide. The well known moth balls are naphthalene.

**Isomerism of the substitution products of naphthalene.**



The number of substitution products obtained from naphthalene is much greater than that obtained from benzene and corresponds with the number theoretically possible for the above formula. Two series of monosubstitution products are possible according as the  $\alpha$ - or  $\beta$ -hydrogen atoms are replaced, and both are known. Those in which the hydrogens 1, 4, 5, or 8 are replaced are called  $\alpha$ -derivatives, while those resulting from the replacement of 2, 3, 6, or 7 are designated  $\beta$ -derivatives. For the disubstitution products, where the substituents are the same, the number of isomers is 10, while it is 14 when they are different. The 10 isomers are designated by the numbers: 1,2; 1,3; 1,4; 1,5; 1,6;

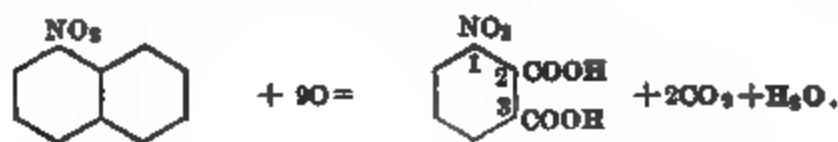
1,7; 1,8; 2,3; 2,6; and 2,7. *Ten dichloronaphthalenes are known, and the structure of each has been determined.* In the case of the  $\alpha$ - and  $\beta$ -naphthylaminemonosulphonic acids,  $\text{H}_2\text{N}\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ , the 14 isomers are all known, and the same is true of the 14 isomeric trichloronaphthalenes predicted by the theory. The substitution of all the hydrogen atoms in naphthalene by different substituents would theoretically give rise to 10,766,600 derivatives. Disubstitution products in which the substituents are in the 1,8 positions are called "peri" compounds. They resemble the ortho derivatives of benzene and naphthalene in many respects, *e.g.*, peri-naphthalenedicarboxylic acid,



forms an anhydride just as *o*-phthalic acid does, and hence is called naphthalic acid. It is made by the oxidation of acenaphthene, a constituent of coal-tar.

The method of determining the position of the substituents in naphthalene is similar to that used in the benzene series. For example, the mononitronaphthalene which results from the direct nitration of naphthalene and which was originally called  $\alpha$ -nitronaphthalene merely to distinguish it from its isomer,  $\beta$ -nitronaphthalene (499) obtained from  $\beta$ -naphthylamine, can be converted into  $\alpha$ -naphthol in the same way that nitrobenzene is converted into phenol (351). The position of the hydroxyl group in  $\alpha$ -naphthol is fixed by its synthesis from  $\gamma$ -phenylisocrotonic acid (494). Therefore, the nitro group in  $\alpha$ -nitronaphthalene must occupy one of the positions 1, 4, 5, or 8, and in  $\beta$ -nitronaphthalene, 2, 3, 6, or 7. Any monosubstitution product that can be converted into  $\alpha$ -naphthol or  $\alpha$ -nitronaphthalene, or can be made from these substances, is called an  $\alpha$ -compound, and this fixes the structure, while its isomer must be the  $\beta$ -compound. Another method consists in the oxidation of the naphthalene derivative to a benzene derivative of known

structure. Thus  $\alpha$ -nitronaphthalene gives the 1,2,3-nitrophthalic acid on oxidation:—



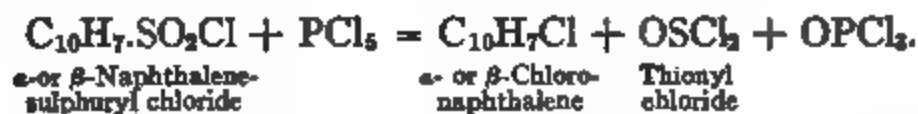
and must have the nitro group in one of the positions 1, 4, 5, or 8.

#### SUBSTITUTION PRODUCTS OF NAPHTHALENE

**Homologues of naphthalene**, methyl, ethyl, and propyl derivatives, etc., are unimportant. They can be made synthetically by the Friedel and Crafts method or by other methods used in preparing the homologues of benzene.  $\alpha$ -Methylnaphthalene (b. p.  $240^\circ - 242^\circ$ ), and  $\beta$ -methylnaphthalene (m. p.  $32^\circ$ ), are both present in coal tar. On oxidation they give the corresponding  $\alpha$ -naphthoic or  $\beta$ -naphthoic acid, compounds which resemble benzoic acid very closely in their properties. They are both converted into naphthalene when distilled with lime.

$\alpha$ -Chloronaphthalene,  $\text{C}_{10}\text{H}_7\text{Cl}$  ( $\alpha$ ), and  $\alpha$ -bromonaphthalene,  $\text{C}_{10}\text{H}_7\text{Br}$  ( $\alpha$ ), are formed by the action of chlorine or bromine on naphthalene in the presence of iron as a catalyst. 1-Chloronaphthalene is a fluid boiling at  $263^\circ$ . 1-Bromonaphthalene is also liquid and boils at  $279.5^\circ$ . Addition products, such as naphthalene dichloride,  $\text{C}_{10}\text{H}_8\text{Cl}_2$ , and naphthalene tetrachloride,  $\text{C}_{10}\text{H}_8\text{Cl}_4$ , similar to naphthalene dihydride and tetrahydride (495, 496), are formed in the cold when no carrier is present. When heated or treated with bases these substances lose hydrochloric acid, giving monochloro- and dichloronaphthalenes. The  $\beta$ -monohalogen derivatives can not be obtained by direct action of the halogens on naphthalene, but are prepared from  $\beta$ -compounds, such as  $\beta$ -naphthol and  $\beta$ -naphthylamine, by the methods used in the benzene series to replace hydroxyl and the amino group by a halogen. The monohalogen derivatives of naphthalene, both  $\alpha$ - and  $\beta$ -, can be prepared readily from the  $\alpha$ - and  $\beta$ -naphthalenesulphonic acids (499) by treating them with phosphorus pentachloride or pentabromide. The chlorides or bromides of the sulphonic acids are first formed, and these by

the further action of the phosphorus compounds give monohalogen derivatives of naphthalene:—



This reaction, which is peculiar to the naphthalene series, also takes place with derivatives of the sulphonic acids. 1-Chloronaphthalene is used in the preparation of chlorosulphonic acids of naphthalene and in making *Naphthalene green V*.

$\alpha$ -Nitronaphthalene,  $\text{C}_{10}\text{H}_7\text{NO}_2(\alpha)$ , is formed by the direct nitration of naphthalene with mixed acid at  $45^\circ$ – $50^\circ$ . No  $\beta$ -product is formed even when the nitration is carried out at a higher temperature (see Naphthalenesulphonic acids below). It crystallizes from alcohol in yellow needles that melt at  $61^\circ$ . Its boiling point is  $304^\circ$ . It dissolves in concentrated sulphuric acid with a blood-red color and when nitrated in this solution gives 1,5- and 1,8-dinitronaphthalene. It is oxidized by chromic acid to nitrophthalic acid (1,2,3) and gives  $\alpha$ -naphthylamine on reduction. It is poisonous. When treated with phosphorus pentachloride, the nitro group is eliminated and  $\alpha$ -chloronaphthalene is formed. This is a reaction peculiar to the naphthalene series. It does not take place in the benzene series. Di-, tri-, and tetranitronaphthalenes are used in the manufacture of explosives. Nitronaphthalene is used in the preparation of  $\alpha$ -naphthylamine and of 1-nitronaphthalene-5-sulphonic acid and of other intermediates.

$\beta$ -Nitronaphthalene is made from  $\beta$ -naphthylamine hydrochloride by diazotizing and treating the diazonium salt with sodium nitrite in the presence of cuprous oxide:—



It crystallizes in yellow needles that melt at  $79^\circ$  and have an odor similar to that of cinnamon. When reduced it gives  $\beta$ -naphthylamine, and this gives  $\beta$ -naphthol when its salt is diazotized and boiled with water.

Naphthalenesulphonic acids,  $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$ , are formed by sulphonation of naphthalene. The 1-acid results in larger

quantity at lower temperatures, the 2-acid at higher temperatures. Thus at  $100^{\circ}$  with concentrated sulphuric acid 95 per cent of the 1-acid and 5 per cent of the 2-acid are formed, while at  $160^{\circ}$ , 18 per cent of the 1-acid and 82 per cent of the 2-acid are obtained. They are separated by recrystallization of the calcium salts, the calcium salt of the 2-acid being more difficultly soluble in water, and are converted into the sodium salts by means of sodium carbonate. From the sodium salts  $\alpha$ - and  $\beta$ -naphthols are obtained by fusing with alkalis:—



and the  $\alpha$ - and  $\beta$ -cyannaphthalenes by fusing with sodium cyanide:—



These cyannaphthalenes give the two naphthoic acids (498) when hydrolyzed. The difference in the conduct of the two naphthalenesulphonic acids towards sodium amalgam is important. The sulfoxyl group in the  $\alpha$ -position is replaced by hydrogen, while in the  $\beta$ -position it is unattacked. The  $\alpha$ -acid is also converted into naphthalene by boiling with dilute sulphuric acid,



while the  $\beta$ -acid undergoes no change.

**Naphthols,  $\text{C}_{10}\text{H}_7\text{OH}$ .**— $\alpha$ - and  $\beta$ -Naphthols are present in coal tar, but are always made from the two monosulphonic acids by fusing with alkalis. They can also be made from the two naphthylamines by diazotizing and boiling their diazonium salts with water.

$\alpha$ -Naphthol is sometimes made on the large scale from  $\alpha$ -naphthylamine by heating it with dilute sulphuric acid in an autoclave to  $200^{\circ}$ :—



This method gives  $\alpha$ -naphthol free from even a trace of  $\beta$ -naphthol. It crystallizes in monoclinic needles, which melt at

94°. It boils at 278°–280°, is only slightly soluble in water, but dissolves readily in alcohol, ether, and benzene. With ferric chloride it gives a violet color and a flocky precipitate. It has an odor somewhat like that of phenol and acts chemically like phenol, although the hydroxyl group reacts more readily than that in phenol. For example, it is readily converted into naphthylamine by heating with the zinc chloride or the calcium chloride compound of ammonia:—



and is converted into the ethyl ether,  $\text{C}_{10}\text{H}_7\text{OC}_2\text{H}_5$ , merely by boiling with alcohol and a mineral acid. This ether, curiously enough, although it does not contain a free hydroxyl group, combines with diazonium salts in the same way that  $\alpha$ -naphthol does to form azo compounds:—



$\alpha$ -Naphthol is used in the preparation of a number of dyes, but most of it is converted into  $\alpha$ -naphtholsulphonic acids, which are very important dyestuff intermediates. It is also used to prepare *Martius yellow* and *Naphthol yellow S*.

**$\alpha$ -Tetrahydro- $\alpha$ -naphthol**,  $\text{HOC}_6\text{H}_3$  , formed by

reducing  $\alpha$ -naphthol in solution in amyl alcohol with sodium, shows in its chemical conduct a very close resemblance to phenol, e.g., it is soluble in alkalies and is precipitated from this solution by carbon dioxide, just as phenol is. Like phenol it also combines with diazonium salts to form hydroxyazo compounds. It is called “aromatic”-tetrahydro- $\alpha$ -naphthol, abbreviated as shown above, to indicate that it acts like an aromatic compound.

$\beta$ -Naphthol is always made synthetically from naphthalene-2-sulphonic acid by fusing with caustic soda. It crystallizes in nearly inodorous, monoclinic leaflets that melt at 123°, and it boils at 285°–286°. It sublimes very readily and is volatile with superheated steam. It is difficultly soluble in cold water, more readily in hot, and in ether, alcohol, and benzene. Ferric



chloride gives first a faint green color and then a white flocculent precipitate. Like  $\alpha$ -naphthol the  $\beta$ -compound is readily converted into ethers with alcohols and hydrochloric acid.

**$\beta$ -Naphthylmethyl ether**,  $C_{10}H_7OCH_3$ , has an odor similar to that of neroli oil. It is made synthetically on the large scale and is used in perfumery under the name, *nerolin*.

With ammonia, or more readily with ammonium sulphite and ammonia, naphthol is converted into  $\beta$ -naphthylamine:—



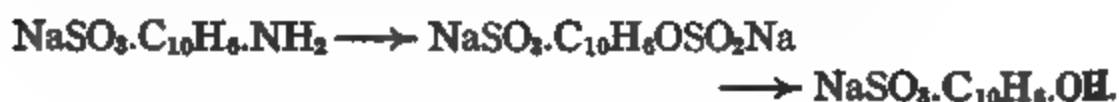
and this is the technical method for the production of  $\beta$ -naphthylamine.

**$\alpha$ -Tetrahydro- $\beta$ -naphthol**,  $C_{10}H_{12}$   $\begin{matrix} \swarrow CH_2.CHOH \\ \searrow CH_2.CH_2 \end{matrix}$ , is formed to-

gether with a small amount of the  $\alpha$ -tetrahydro product by the reduction of  $\beta$ -naphthol with sodium and amyl alcohol. It acts like a secondary alcohol, while the  $\alpha$ -compound acts like a phenol. It is called "alicyclic" (abbreviated to  $\alpha$ c) to show that it acts like the aliphatic and cyclic compounds.

Enormous quantities of  $\beta$ -naphthol are used in making azo dyes and dyestuff intermediates. Large quantities are also converted into  $\beta$ -naphthylamine. About 12 million pounds were made in the United States in 1920.

**Naphtholsulphonic acids** are obtained by sulphonation of the naphthols or from the naphthylaminesulphonic acids. Thus, 1-naphthol-4-sulphonic acid was for a long time made by diazotizing naphthionic acid (1-naphthylamine-4-sulphonic acid) and boiling the diazonium salt with water. This method is no longer used, since naphthionic acid can be more readily converted into the hydroxy acid by heating with sodium bisulphite and an alkali. Ammonia splits off, and the sodium salt of a sulphurous acid ester of 1-naphthol-4-sulphonic acid is first obtained and then saponified by the alkali:—



The acid is also made technically by heating 1-chloronaphthalene-4-sulphonic acid with dilute caustic soda solution under pressure to 200°, when the chlorine is replaced by the hydroxyl group.  $\alpha$ -Naphthol gives a mixture of the ortho and para acids when sulphonated. If, however, the hydroxyl group is rendered inactive, only the para acid is formed. Thus  $\alpha$ -naphthylethyl ether gives only the 4-sulphonic acid. 1-Naphthol-4-sulphonic acid is used, in the form of its sodium salt, in the manufacture of azo-dyes and is known as *Neville and Winther's acid*. The 2,6- and 2,8- $\beta$ -naphtholsulphonic acids made by sulphonating  $\beta$ -naphthol are also important dyestuff intermediates. The first is called *Schäffer's acid* and the second *crocein acid*, because of its use in the manufacture of crocein scarlet (made by diazotizing aminoazobenzenesulphonic acid and combining it with the crocein acid in alkaline solution). The  $\beta$ -naphtholdisulphonic acids (2,3,6 and 2,6,8), known in the form of their sodium salts as *R-salt* and *G-salt*, because one gives red (rot) and the other yellow (gelb) azo dyes with diazonium salts, are important dyestuff intermediates. *Chromotropic acid* (1,8-dihydroxynaphthalene-3,6-disulphonic acid) made from the 1-amino-8-naphthol-3,6-disulphonic acid (*H-acid*), by heating with a concentrated solution of caustic potash, is also of technical importance.

**Nitronaphthols** analogous to the nitrophenols are formed by the nitration of the naphthols. For example, 2,4-dinitro- $\alpha$ -naphthol is made by nitrating  $\alpha$ -naphthol mono- or disulphonic acid, the sulphonic acid groups being displaced by the nitro groups, and 2,4-dinitro- $\alpha$ -naphthol-7-sulphonic acid by nitrating  $\alpha$ -naphtholtrisulphonic acid (1,2,4,7). In this case the sulphonic acid groups in positions 2 and 4 are replaced by nitro groups, while that in 7 is not attacked. The sodium salts of these nitro compounds are yellow dyes known as *Martius yellow* and *Naphthol yellow S*, respectively.

**Aminonaphthols** are made by the reduction of the nitronaphthols, and like the aminophenols readily undergo oxidation in the air. The 1-amino-8-naphthol-3,6-disulphonic acid is known as *H-acid* and is largely used in the manufacture of

azo dyes. The sodium salt of the 1-amino-2-naphthol-6-sulphonic acid, known as *eikonogen*, is used as a photographic developer.

**$\alpha$ -Naphthylamine**,  $C_{10}H_7NH_2(\alpha)$ , is made on the large scale by reducing  $\alpha$ -nitronaphthalene in the same way that aniline is made from nitrobenzene. It can also be made by heating naphthalene to its boiling point with sodium amide,  $NaNH_2$ , hydrogen being evolved. It crystallizes from alcohol in colorless needles, melts at  $50^\circ$ , and boils at  $301^\circ$ . It is very difficultly soluble in water, has a disagreeable, fecal odor, and sublimes readily. Like aniline it turns brown in the air, due to oxidation. Chromic acid oxidizes it to  $\alpha$ -naphthaquinone (506). Its hydrochloride is sparingly soluble in water and is converted into the diazonium salt,  $C_{10}H_7N_2Cl$ , by the action of nitrous acid. When boiled with water this gives  $\alpha$ -naphthol, and it combines with phenols or naphthols and with aromatic amines, in the same way that the benzene diazonium salts do, to form azo dyes. When heated with sodium amide (and naphthalene) to  $230^\circ$  it gives 1,5-naphthylenediamine,  $C_{10}H_6(NH_2)_2$ .

$\alpha$ -Naphthylamine is used in making dyes and intermediates. Most of it is converted into naphthionic acid. Over 5 million pounds were made in the United States in 1920.



is formed by the action of sodium on the amyl alcohol solution of  $\alpha$ -naphthylamine. It resembles aniline in its chemical conduct, e.g., it can be diazotized, and the diazonium salt is converted into *ar*-tetrahydro- $\alpha$ -naphthol by boiling with water.

**$\beta$ -Naphthylamine**,  $C_{10}H_7NH_2(\beta)$ , is made on the large scale by heating  $\beta$ -naphthol (501) with 20 per cent ammonia and ammonium sulphite under pressure. It crystallizes in leaflets, melts at  $112^\circ$ , boils at  $306^\circ$ , and differs from  $\alpha$ -naphthylamine in being odorless. It is more stable than the  $\alpha$ -compound and is not colored by oxidizing agents.

$\beta$ -Naphthylamine is used in making dyes and intermediates. It is not as important as the  $\alpha$ -compound.



benzidine, is a dimethyl derivative of Congo red containing a methyl group attached to each of the benzene residues of the diphenyl group. A few of the simpler azo dyes of this series are:—

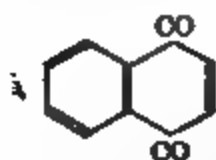
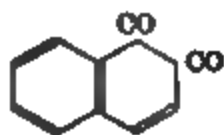
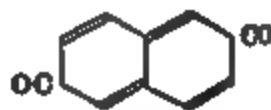
**Orange II**,  $\text{NaSO}_3 \cdot \text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_6\text{OH}(\beta)$ , made by diazotizing sulphanilic acid and combining it in alkaline solution with  $\beta$ -naphthol, is an important azo dye containing a benzene and a naphthalene residue. Nearly 2,000,000 pounds were made in the United States in 1920.

**Ponceau, 2 R**,  $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{N}=\text{N} \cdot \text{C}_{10}\text{H}_6\text{OH}(\text{SO}_3\text{Na})_2$ , made from diazotized xylydine hydrochloride and R-salt (503) is an important red azo-dye. Over 1,000,000 pounds were made in the United States in 1920.

**Fast red**,  $\text{NaSO}_3 \cdot \text{C}_{10}\text{H}_6-\text{N}=\text{N}-\text{C}_{10}\text{H}_6(\text{OH}) \cdot \text{SO}_3\text{Na}$ , made by diazotizing naphthionic acid and combining it with 1,4-naphthol-sulphonic acid, is an example of a red azo dye containing two naphthalene residues.<sup>1</sup> Nearly 500,000 pounds were made in the United States in 1920.

**Quinones of the naphthalene series.**—Three isomeric quinones,  $\text{C}_{10}\text{H}_6\text{O}_2$ , are known. They are called  $\alpha$ -,  $\beta$ -, and *amphi*-according to the position of the ketone groups.

**$\alpha$ -Naphthaquinone** is made by the oxidation of naphthalene,  $\alpha$ -naphthylamine, 1,4-dihydroxynaphthalene and other disubstitution products of naphthalene having the groups in the 1,4 position, with chromic acid. It crystallizes in yellow, triclinic needles that melt at  $125^\circ$ , and resembles ordinary *p*-benzoquinone closely in its properties. It has a similar odor, is volatile with steam, and gives a dioxime with hydroxylamine. It is reduced by sulphurous acid to 1,4-dihydroxynaphthalene and therefore has the two carbonyl groups in the 1,4 position, or it is a para quinone (I):—

I.  $\alpha$ -NaphthaquinoneII.  $\beta$ -Naphthaquinone

III. amphi-Naphthaquinone

<sup>1</sup> See *Synthetic Dyestuffs*, by J. C. Caine and J. T. Thorpe, for further information regarding these dyes.

**$\beta$ -Naphthaquinone** resembles *o*-benzoquinone in that it is not volatile with steam and has no odor. It is obtained by the oxidation of 1-amino-2-naphthol or of 1,2-dihydroxynaphthalene, and is reduced to this latter compound by sulphurous acid. Hence it is a 1,2 or ortho quinone (II). It crystallizes in red needles, which decompose at 115°, and forms a dioxime with hydroxylamine.

**amphi-Naphthaquinone** or **2,6-naphthaquinone** is made by oxidizing 2,6-dihydroxynaphthalene in benzene solution with lead peroxide and yields this dihydroxynaphthalene on reduction. Hence the structure (III). It crystallizes in yellowish red prisms, is not volatile with steam and has no odor. It is a strong oxidizing agent.

**Naphthazarin**, **5,6-dihydroxy- $\alpha$ -naphthaquinone**, is a dye that resembles alizarin, whence the name. It is made from 1,5-dinitronaphthalene by heating it with a solution of sulphur in fuming sulphuric acid. It is ordinarily called *Alizarin black* in the trade and is a valuable mordant dye.

**Nitroso- $\beta$ -naphthol** is  **$\beta$ -naphthaquinone- $\alpha$ -oxime**. It is made by the action of nitrous acid on  $\beta$ -naphthol. (Compare with the formation of nitrosophenol or quinone monoxime.) It crystallizes in orange brown prisms that melt at 110°. It is used in analytical chemistry, especially to detect and determine cobalt and as a dye under the name *Gambine Y*.

### QUINOLINE AND ISOQUINOLINE AND THEIR DERIVATIVES

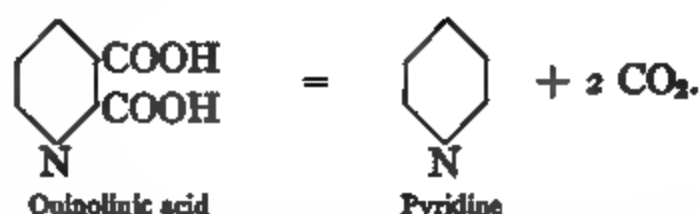
Quinoline and isoquinoline are basic substances, resembling pyridine, found in coal tar and bone oil. They are of importance because of their close connection with the alkaloids. Thus, quinine gives quinoline,  $\alpha$ -methylquinoline (lepidine), and *p*-methoxyquinoline, when fused with caustic potash, and papaverine gives derivatives of isoquinoline.

Quinoline,  $C_9H_7N$ , has been isolated from coal tar and bone oil. It is difficult, however, to obtain it pure from these sources or from the alkaloids. When required pure it is usually made synthetically by Skraup's method (509,510). It is a colorless,

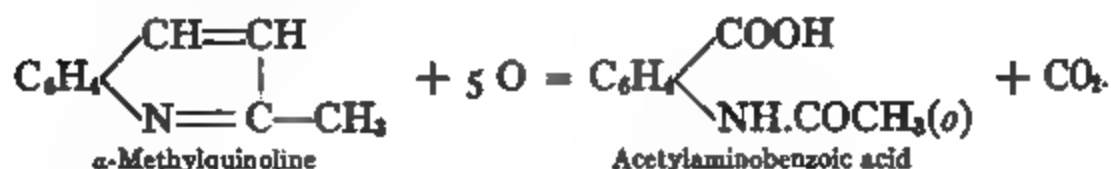
highly refracting liquid, having a very characteristic odor. It boils at  $238^{\circ}$ , solidifies at  $-22.6^{\circ}$  and is heavier than water. It is a monacid, tertiary base like pyridine, and forms well characterized salts with acids. The dichromate  $(C_9H_7N)_2H_2Cr_2O_7$ , is difficultly soluble in water. It combines with methyl iodide just as

pyridine does, forming methyl quinolonium iodide,  $C_9H_7N \begin{matrix} \diagup CH_3 \\ \diagdown I \end{matrix}$ .

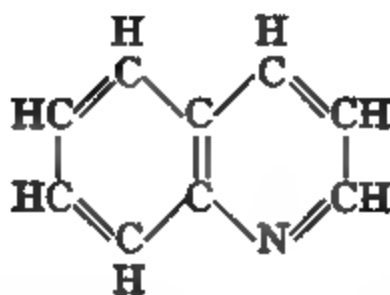
When oxidized with potassium permanganate quinoline gives quinolinic acid,  $C_8H_5N(COOH)_2$ , just as naphthalene gives phthalic acid. Like phthalic acid, quinolinic acid yields an anhydride when heated, and hence the two carboxyl groups are in the ortho position to each other. When distilled with lime quinolinic acid gives pyridine, just as phthalic acid gives benzene:—



Quinolinic acid is, therefore, a pyridinedicarboxylic acid with the carboxyl groups in the ortho position to each other. It has been shown to be  $\alpha,\beta$ -pyridinedicarboxylic acid, as it loses carbon dioxide and is converted into  $\beta$ -pyridinemonocarboxylic acid (nicotinic acid) when heated, and has been made by the oxidation of  $\alpha,\beta$ -dimethylpyridine. Quinoline, hence, contains a pyridine ring. When  $\alpha$ -methylquinoline, which can be made from quinoline, is oxidized it gives an acetyl derivative of *o*-aminobenzoic acid:—

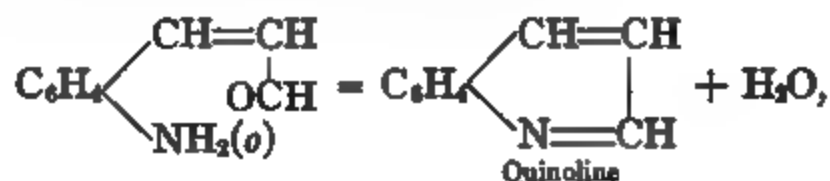


Hence quinoline must also contain a benzene ring. From these facts it is concluded that quinoline contains a benzene ring and a pyridine ring with two ortho carbon atoms in common:—

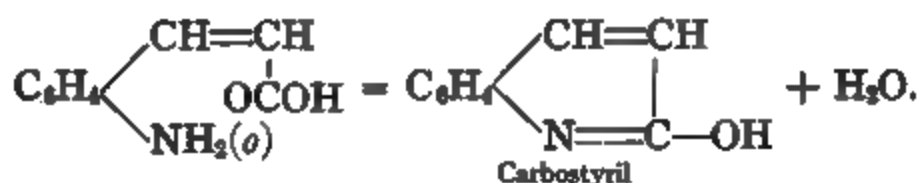


It will be seen from the above formula that quinoline is naphthalene in which one of the CH-groups in the  $\alpha$ -position (1, 4, 5 or 8) is replaced by nitrogen. It therefore bears the same relation to naphthalene that pyridine bears to benzene. This formula has been confirmed by the following syntheses from aniline or ortho substitution products of aniline:—

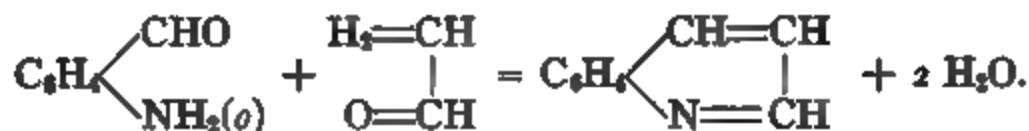
1. *o*-Aminocinnamic aldehyde, obtained by the reduction of *o*-nitrocinnamic aldehyde, loses water and gives quinoline,



while carbostyryl ( $\alpha$ -hydroxyquinoline (512)) is formed from *o*-aminocinnamic acid:—



2. *o*-Aminobenzaldehyde condenses very readily with aldehydes or ketones in the presence of dilute caustic soda to form quinoline and its derivatives:—

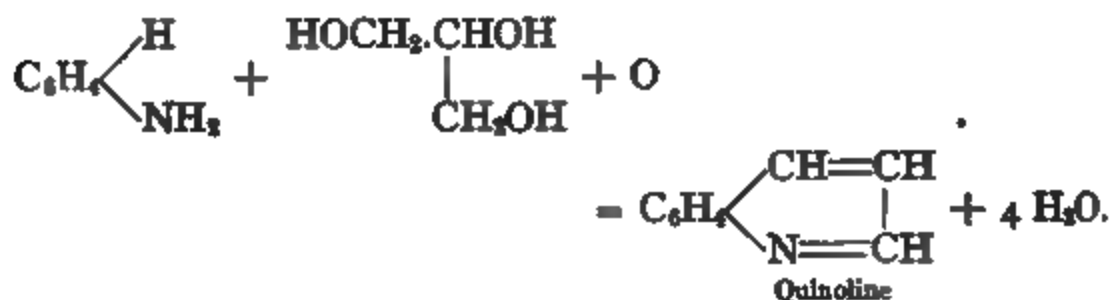


Acetone gives  $\alpha$ -methylquinoline (quinaldine).

3. The most important synthesis of quinoline and its derivatives and the one used to prepare these substances in the pure state is that due to Skraup. It consists in heating aniline,



glycerol, and concentrated sulphuric acid with an oxidizing agent, such as nitrobenzene or arsenic acid : —

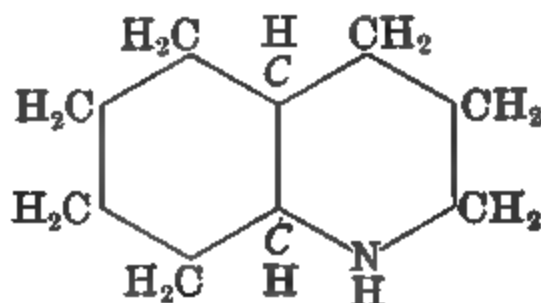


Acrolein,  $\text{CH}_2=\text{CH}.\text{CHO}$ , is formed here as an intermediate product and combines with the aniline to form  $\beta$ -phenylamino-propionic aldehyde,  $\text{C}_6\text{H}_5.\text{NH}.\text{CH}_2.\text{CH}_2.\text{CHO}$ , which is then oxidized to quinoline. Homologues of aniline give homologues of quinoline, and derivatives of aniline give derivatives of quinoline in which the substituting group is in the benzene portion of the quinoline.

The hydrogen addition products are also in accord with the above formula for quinoline. It takes up four hydrogen atoms

quite readily, forming quinoline tetrahydride,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CH}_2.\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NH}.\text{CH}_2 \end{array}$ ,

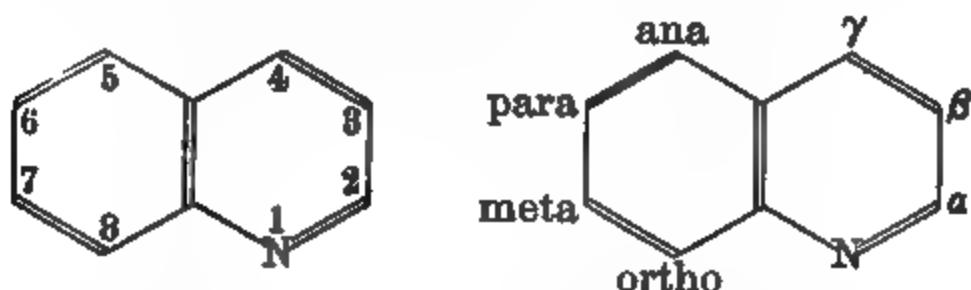
which acts as a secondary base. The N-methyl derivative of this base is *kairolin*, which is used as an antipyretic. The final product of the reduction of quinoline is quinoline decahydride : —



This is a strong, secondary base having the character of an aliphatic amine. It absorbs carbon dioxide from the air and has a stupefying odor similar to that of conine. It has been separated into its optically active modifications.

The number of substitution products obtained from quinoline

is very large and is in accord with the number theoretically possible. Thus, there are 7 monosubstitution products possible, as will be seen by an examination of the formula:—



A substituting group or atom may take the place of any one of the hydrogen atoms indicated by the numbers 2, 3, 4, 5, 6, 7, 8, each of which bears a different relation to the nitrogen atom. *Seven monomethyl derivatives are known*, and these are converted into the seven possible monocarboxylic acids by oxidation. The seven monochloro derivatives are also all known. Another method of designating the hydrogen atoms in quinoline is shown above. Those in the pyridine ring are marked  $\alpha$ ,  $\beta$ , and  $\gamma$  as in pyridine, while those in the benzene ring are designated ortho-, meta-, para-, and ana-.

#### HOMOLOGUES AND DERIVATIVES OF QUINOLINE

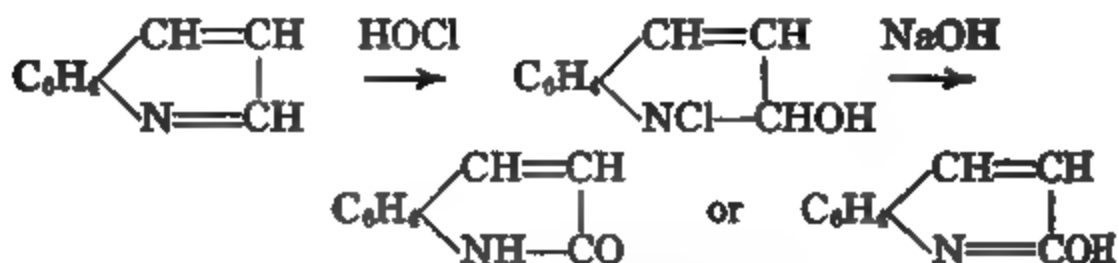
**Quinaldine**,  $\alpha$ -methylquinoline,  $C_9H_8(CH_3)N$ , is present in coal tar and in the crude quinoline obtained from coal tar. It is a liquid having the odor of quinoline and boiling at  $246^\circ$  to  $248^\circ$ . It has been made synthetically (see method 2 above) from acetone, and also from quinoline by the method used to make  $\alpha$ -methylpyridine (439) from pyridine. When oxidized with chromic acid it gives quinaldinic acid,  $C_9H_7N.CO_2H$ , which is converted into quinoline by heating with lime. The  $\alpha$ -position of the methyl group is proved by the formation of acetyl- $\alpha$ -aminobenzoic acid by oxidation with potassium permanganate (508).

**Lepidine**,  $\gamma$ -methylquinoline,  $C_9H_8(CH_3)N$ , is present in coal tar and is formed by distilling cinchonine with caustic potash. It boils at  $258^\circ$ – $260^\circ$ . The position of the methyl group

follows from its oxidation with potassium permanganate to  $\gamma$ -methylpyridine- $\alpha$ - $\beta$ -dicarboxylic acid.

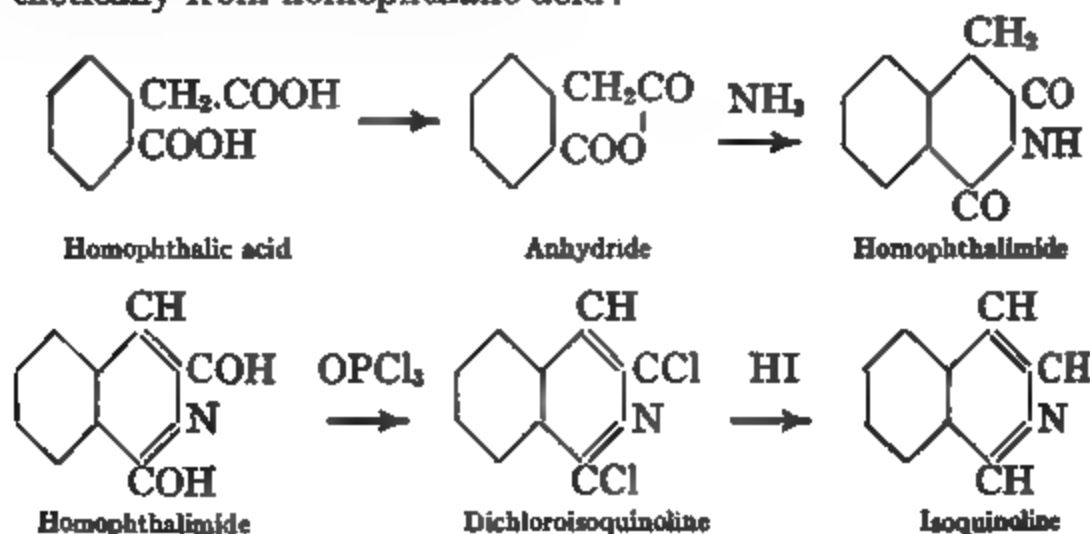
***o*-Hydroxyquinoline**,  $C_8H_6(OH)N$ , is made from *o*-aminophenol by Skraup's synthesis, and also from quinoline-*o*-sulphonic acid by fusing with alkalis. It crystallizes from alcohol in colorless prisms, melts at  $75^\circ$ – $76^\circ$  and resembles  $\alpha$ -naphthol, *e.g.* it gives *o*-aminoquinoline, when heated with the ammonia compound of zinc chloride.

**$\alpha$ -Hydroxyquinoline**, carbostyryl, is formed by the elimination of water from the *cis*-form of *o*-aminocinnamic acid (480). It is more readily prepared from quinoline by the action of bleaching powder and an alkali:—



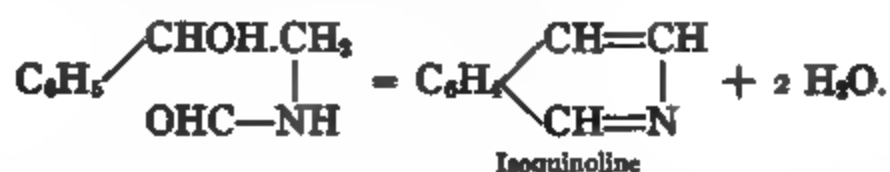
It crystallizes from water with a molecule of water, from alcohol in the anhydrous form, which melts at  $199^\circ$ – $200^\circ$ . It acts as a tautomeric substance (see formulas above) and gives both N- and O-alkyl ethers. With phosphorus pentachloride it is converted into  $\alpha$ -chloroquinoline, and this on reduction with hydriodic acid yields quinoline.

**Isoquinoline** was first found in coal tar and then made synthetically from homophthalic acid:—



Isoquinoline is also formed directly from homophthalimide by distillation with zinc dust in an atmosphere of hydrogen.

A simpler synthesis is that from formaminomethylphenyl carbinol by the loss of water:—



The constitution of isoquinoline as a derivative of naphthalene in which a  $\beta$ -CH group is replaced by nitrogen follows from the syntheses, and from the fact that on oxidation it gives phthalic acid and cinchomeronic acid, *i.e.* an ortho dicarboxylic acid of benzene and an ortho dicarboxylic acid of pyridine ( $\beta,\gamma$ -acid, isomeric with quinolinic acid). Isoquinoline melts at  $24^\circ$ – $25^\circ$  and boils at  $240.5^\circ$ . Its odor is similar to that of benzaldehyde. It is a basic substance and resembles quinoline in its chemical conduct. The alkaloids, papaverine, narcotine, laudanosine, and hydrastine are derivatives of isoquinoline or its tetrahydride.

## CHAPTER XX

### ANTHRACENE AND PHENANTHRENE AND SOME OF THEIR DERIVATIVES

**Anthracene** (Gr. *anthrax*, coal),  $C_{14}H_{10}$ , together with its isomer, phenanthrene, and other hydrocarbons and carbazole, is present in the anthracene oil obtained in the distillation of coal tar.<sup>1</sup> Coal tar is the only source of anthracene, although it contains only 0.2 to 0.5 per cent of this hydrocarbon. It is separated from the anthracene oil by slow cooling and centrifuging the crude anthracene which crystallizes out. This product, which contains from 25 to 40 per cent anthracene, is further purified by washing with solvent naphtha, in which anthracene is practically insoluble, to remove oil and the major portion of the phenanthrene and other hydrocarbons present. The dried material (50–60 per cent anthracene) is then fused with a mixture of caustic potash and caustic soda at  $260^{\circ}$ – $270^{\circ}$ , and subjected to sublimation in superheated steam. This removes the carbazole (492) which forms a non-volatile sodium or potassium salt,  $(C_6H_4)_2=NK$ . The sublimed anthracene is again extracted with solvent naphtha to remove the remainder of the phenanthrene, etc., and resublimed. This product (90–95 per cent anthracene) is then converted into anthraquinone by oxidation. The determination of the amount of pure anthracene in the crude product is made by oxidizing it with chromic acid to anthraquinone, which is then purified and weighed. This is known as the Höchst anthracene test.

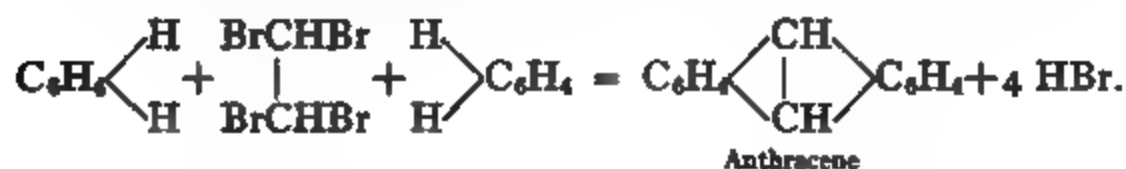
Anthracene crystallizes in colorless, monoclinic plates which when absolutely pure show a bluish fluorescence. It melts at  $213^{\circ}$  and boils at about  $360^{\circ}$ , with slight decomposition. It is insoluble in water and difficultly soluble in most organic solvents. Benzene and its higher homologues dissolve it to some extent at

<sup>1</sup> See *Coal Tar and Ammonia*, by G. Lunge, 5th ed. 1916.

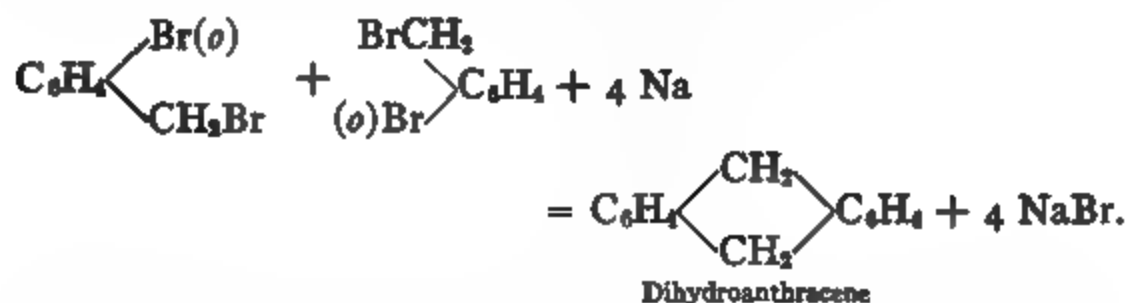
their boiling points. The pure product is best obtained by the reduction of pure anthraquinone. Anthracene forms an addition product with picric acid crystallizing in ruby-red needles that melt at  $138^{\circ}$ . This is used as a test for anthracene. Direct sunlight converts anthracene into a polymeric modification, *dianthracene*,  $C_{28}H_{20}$ , melting at  $243^{\circ}$ . In the dark or when heated to its melting point dianthracene is reconverted into anthracene. Over 700,000 pounds of anthracene (100 per cent) were produced in the United States in 1920, and a considerable quantity was imported. The entire quantity is converted into anthraquinone for the purpose of making the anthraquinone dyes.

The constitution of anthracene has been determined from its syntheses from benzene or ortho derivatives of benzene, some of the more important of which are as follows:—

1. Benzene when heated with symmetrical tetrabromoethane in the presence of aluminium chloride gives anthracene:—

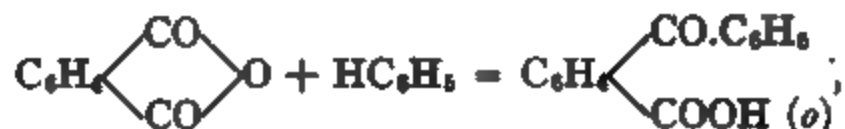


2. *o*-Bromobenzylbromide in solution in ether when treated with sodium gives a mixture of dihydroanthracene and anthracene:—

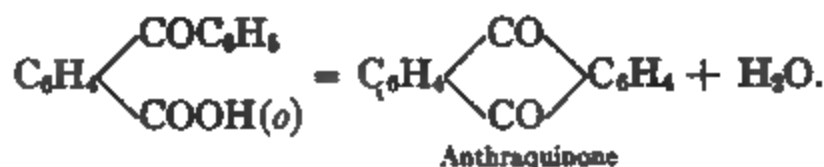


When this mixture is heated on a water bath with sulphuric acid the dihydroanthracene is oxidized to anthracene. That anthracene as well as dihydroanthracene is formed in this reaction is explained by the ease with which dihydroanthracene loses hydrogen and is converted into anthracene.

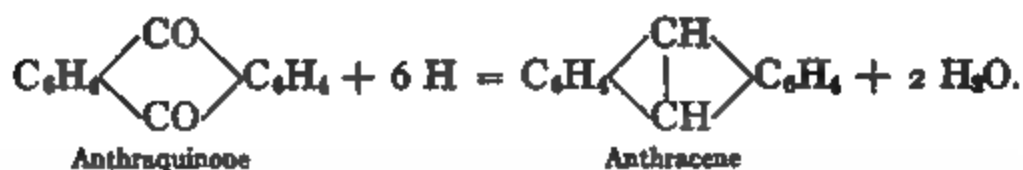
3. Phthalic anhydride combines with benzene in the presence of aluminium chloride to form *o*-benzoylbenzoic acid:—



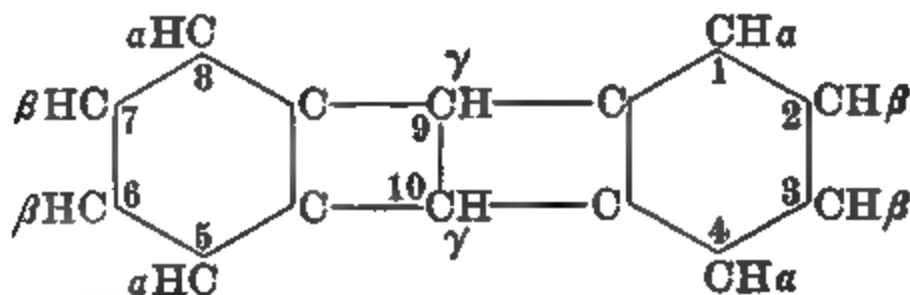
and this yields anthraquinone by the action of sulphuric acid:—



Anthraquinone when heated with zinc dust is reduced to anthracene:—

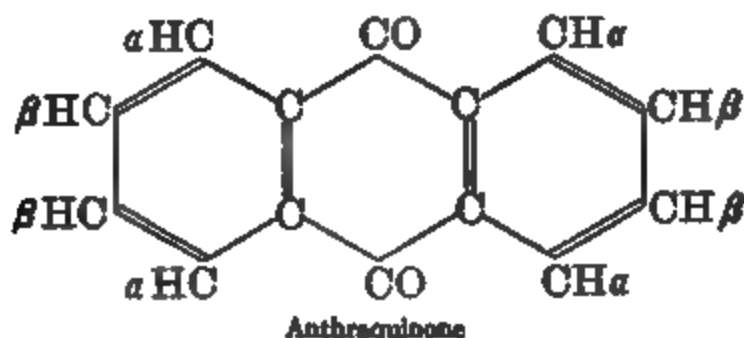


From these syntheses and from the fact that anthracene gives anthraquinone on oxidation, the constitution of which is determined by synthesis 3, it will be seen that anthracene contains two residues of benzene joined by means of the group  $\text{C}_2\text{H}_2$ . According to synthesis 1 these two middle carbon atoms are joined to each other, and according to the other syntheses they take in each benzene residue the ortho position to each other, as shown in the formula below:—



According to this formula there should be three series of mono substitution products possible according as hydrogen atoms  $\alpha$ ,  $\beta$ , or  $\gamma$  are replaced. As a matter of fact three monochloroanthracenes, three monohydroxyanthracenes and three mono-

aminoanthracenes, etc., are all known. When anthracene is oxidized to anthraquinone,



however, it will be seen that the  $\gamma$ -hydrogen atoms disappear and that only two series of mono derivatives,  $\alpha$  and  $\beta$ , are possible. Here again the formula is in accord with the facts. Two monosulphonic acids, two mononitro derivatives, etc., of anthraquinone are known and only two.

The reduction products of anthracene are also in accord with the theory. Dihydroanthracene, whose formula is determined by synthesis 2, is formed very readily from anthracene by reduction with sodium and alcohol. Further reduction with more powerful reducing agents gives  $C_{14}H_{16}$  and finally  $C_{14}H_{24}$ . (Write out the formulas.)

Chlorine and bromine first form  $\gamma$ -addition products with anthracene, such as anthracene dichloride,  $C_6H_4 \begin{array}{c} \text{CHCl} \\ \diagdown \quad \diagup \\ \text{CHCl} \end{array} C_6H_4$ .

Halogen acid then splits off, giving a  $\gamma$ -monohalogen substitution product, e.g.  $C_6H_4 \begin{array}{c} \text{CCl} \\ | \\ \text{CH} \end{array} C_6H_4$ . This takes up more chlorine

to form the addition product,  $C_6H_4 \begin{array}{c} \text{CCl}_2 \\ \diagdown \quad \diagup \\ \text{CHCl} \end{array} C_6H_4$ , from which

by the elimination of hydrochloric acid the 9,10-dichloroanthracene,  $C_6H_4 \begin{array}{c} \text{CCl} \\ | \\ \text{CCl} \end{array} C_6H_4$  results.

Hydroxyanthracenes,  $C_6H_4 \cdot C_2H_2 \cdot C_6H_3OH$ ,  $\alpha$ , and  $\beta$ , are called *anthrols*. They are made by fusing  $\alpha$ - or  $\beta$ -anthracenesulphonic

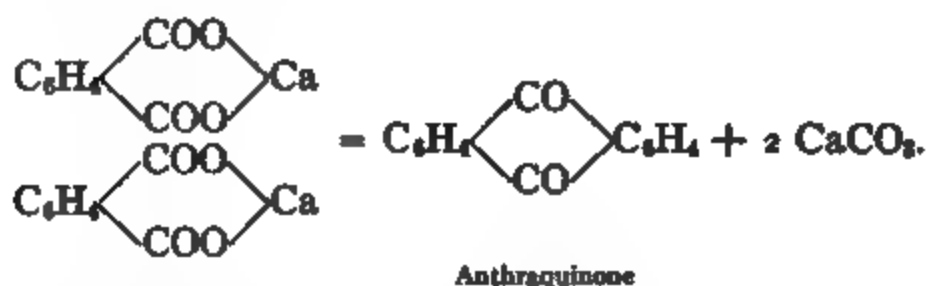


acid with alkali or by reducing  $\alpha$ - or  $\beta$ -hydroxyanthraquinone (521). They resemble the phenols and especially the naphthols in their chemical conduct.

$\gamma$ -Hydroxyanthracene or anthranol is obtained by reducing anthraquinone. (See below.)

The most important derivative of anthracene is anthraquinone.

Anthraquinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_4$ , is formed by the distillation of calcium phthalate:—



This method, which is the one used for making ketones, indicates that anthraquinone is a diketone.

On the large scale two methods are used to make anthraquinone, which is a very important dyestuff intermediate, (1) direct oxidation of anthracene, and (2) synthesis from phthalic anhydride and benzene (516). As phthalic anhydride (416) is made from naphthalene, this is a method for making anthraquinone from naphthalene.

In the oxidation of anthracene two processes are used, (1) oxidation with sodium bichromate and sulphuric acid, and (2) oxidation of the anthracene in the form of vapor with air in the presence of a catalyst, such as vanadium oxide. This method is analogous to that used technically to make phthalic anhydride from naphthalene.

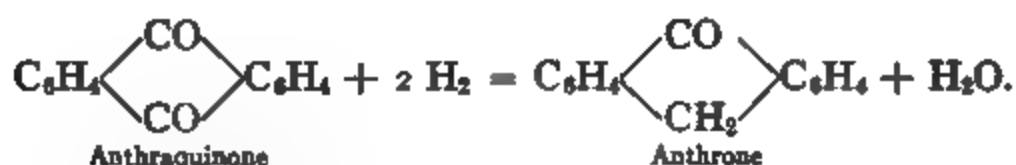
Anthraquinone crystallizes in yellow, orthorhombic prisms which melt at  $285^\circ$  (cor.). It sublimes in yellow needles and boils at  $382^\circ$ . It dissolves when heated with concentrated sulphuric acid at  $100^\circ$  and is precipitated from this solution unwater. This is the method made use of on the large scale to purify anthraquinone. The impurities are converted

into sulphonic acids, which are soluble in water. It is difficultly soluble in most organic solvents, but dissolves in hot glacial acetic acid and benzene. Towards oxidizing agents it is exceedingly stable. Anthraquinone differs from the para quinones of the benzene and naphthalene series in several respects, and exhibits many of the properties of the diketones, e.g. it does not have the characteristic quinone odor, is not volatile with steam, and is not reduced by sulphurous acid. About 540,000 pounds of anthraquinone were produced in the United States in 1920, a considerable part of which was made synthetically from phthalic anhydride and benzene. It is all used in the preparation of the anthraquinone dyes.

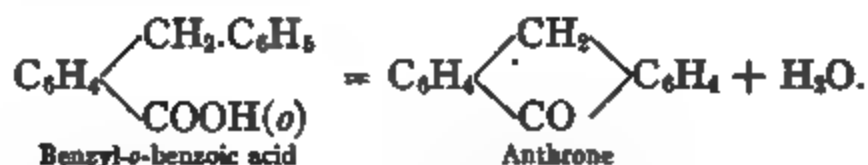
When fused with caustic potash it gives potassium benzoate :—



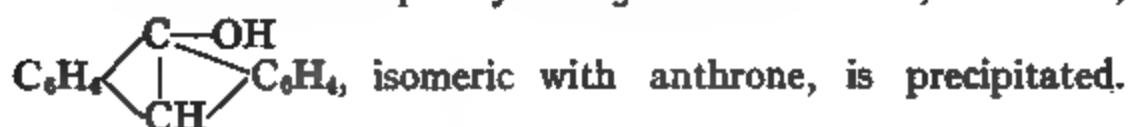
Hydriodic acid reduces it to anthracene and dihydroanthracene. When reduced in glacial acetic acid with tin and hydrochloric acid *anthrone* is formed :—



This substance has also been obtained by the action of sulphuric acid on benzyl-*o*-benzoic acid (made by the reduction of benzoyl-*o*-benzoic acid):—



It forms colorless crystals, melting at 154°–155°, and is insoluble in cold solutions of the alkalis. When heated to boiling with a dilute solution of caustic soda it dissolves. If this solution is cooled quickly to –5° and acidified, *anthranol*,



This substance crystallizes in brownish yellow leaflets, which melt at once when brought into a bath heated to  $120^{\circ}$ . It dissolves in glacial acetic acid with a yellow color. When this solution is boiled the color fades, and on the addition of water anthrone crystallizes out. Anthranol is completely soluble in cold aqueous alkalis, and its solutions in organic solvents show a marked bluish fluorescence, while those of anthrone are non-fluorescent.

Anthraquinone when reduced with zinc dust and caustic soda solution gives *anthrahydroquinol*,  $C_6H_4 \begin{array}{c} \diagup C(OH) \\ | \\ \diagdown C(OH) \end{array} C_6H_4$ . This crys-

tallizes in flat, brown crystals melting at  $180^{\circ}$ , readily soluble in alcohol, the solution having a yellow color and strong greenish fluorescence. Iodine or bromine oxidizes it instantaneously to anthraquinone. It is completely soluble in cold aqueous alkali with a deep red color and readily undergoes oxidation to anthraquinone in this solution by air. It is converted to some extent into its isomer,  $\gamma$ -hydroxyanthrone, in the cold by 3 per cent alcoholic hydrochloric acid.  $\gamma$ -Hydroxyanthrone (oxyanthranol)

$C_6H_4 \begin{array}{c} CO \\ \diagup \diagdown \\ HCOH \end{array} C_6H_4$ , is best made, however, by the hydrolysis of

bromoanthrone,  $C_6H_4 \begin{array}{c} CO \\ \diagup \diagdown \\ HCB r \end{array} C_6H_4$  (made by brominating an-

throne). It crystallizes in yellowish white needles melting at  $167^{\circ}$  which are colorless when powdered. Unlike its isomer, anthrahydroquinol, iodine and bromine are without action on it in the cold and its solutions in organic solvents do not fluoresce. It is also insoluble in cold aqueous alkalis. It is converted into its isomer, anthrahydroquinol, to the extent of 97 per cent by alcoholic hydrochloric acid.

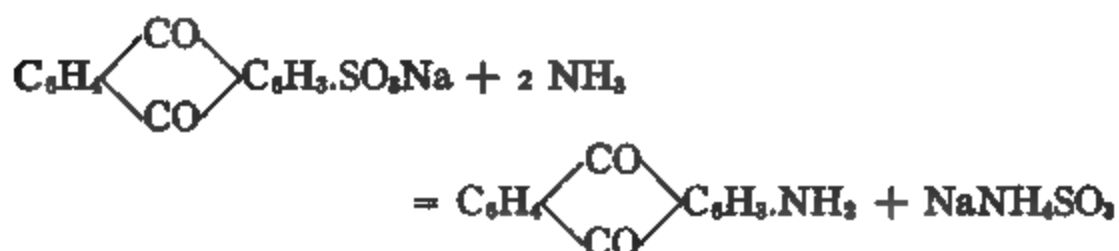
Anthraquinone- $\beta$ -sulphonic acid,  $C_6H_4 \begin{array}{c} CO \\ \diagup \diagdown \\ CO \end{array} C_6H_4 \cdot SO_3H(\beta)$ , is obtained by sulphonating anthraquinone with fuming sulphuric

acid at 160°. Its sodium salt, which is difficultly soluble in cold water and has a silvery luster, is known in the trade as "silver salt."

**Anthraquinone- $\alpha$ -sulphonic acid** is formed by sulphonating anthraquinone in the presence of mercury salts.

**$\alpha$ - and  $\beta$ -Hydroxyanthraquinones** are obtained from these acids by heating them with a 20 per cent solution of caustic soda under pressure.

**2-Aminoanthraquinone** is obtained by heating sodium anthraquinone- $\beta$ -sulphonate with 25 per cent ammonia under pressure:—



It is the substance from which the very valuable *indanthrene* vat dyes are made.<sup>1</sup> These dyes are the fastest and among the most important vat dyes known. Most of them are imported at the present time.

There are ten possible dihydroxyanthraquinones, and all are known. Alizarin is the only one of commercial importance.



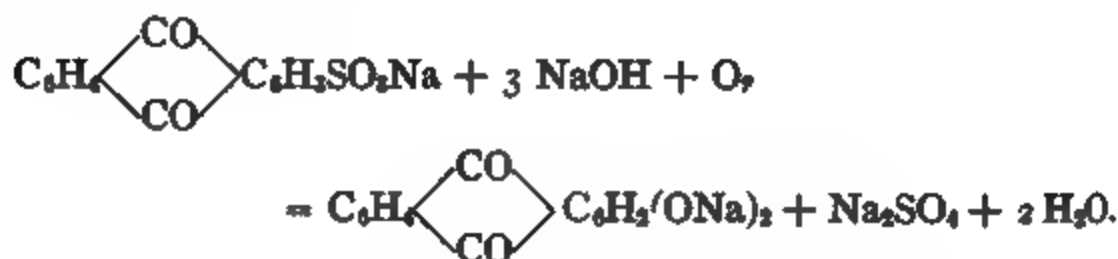
is the chief constituent of the red dye (Turkey red) obtained from madder root (*Rubia tinctorium*) and known for centuries. The dye was not isolated from the madder root, but the whole root was used, after it had been dried and could be ground finely. It is present in madder root as a glucoside, *ruberythric acid*,  $\text{C}_{26}\text{H}_{28}\text{O}_{14}$ , which is hydrolyzed by dilute mineral acids or by the action of an enzyme contained in the madder root, to alizarin and glucose:—



<sup>1</sup> See *Synthetic Dyestuffs*, by J. C. Caine and J. T. Thorpe, 5th ed. 1920, p. 127.

In Europe large tracts of land were devoted to growing madder, especially in Holland and France. The annual production of madder root exceeded in value \$15,000,000. The discovery of the artificial preparation of alizarin from coal tar in 1869, the first of the natural dyes to be made synthetically, destroyed this industry and released the land for the growing of food-crops.

Alizarin is now made on the large scale by heating the sodium salt of anthraquinone- $\beta$ -sulphonic acid with a concentrated solution of caustic soda and some potassium nitrate in an autoclave to 180°:



In this reaction not only is the sulphonic acid group replaced by hydroxyl, but the  $\alpha$ -hydrogen is also oxidized to hydroxyl. The dye is set free from the solution of the sodium salt by an acid and brought into the market in the form of a 20 per cent paste.

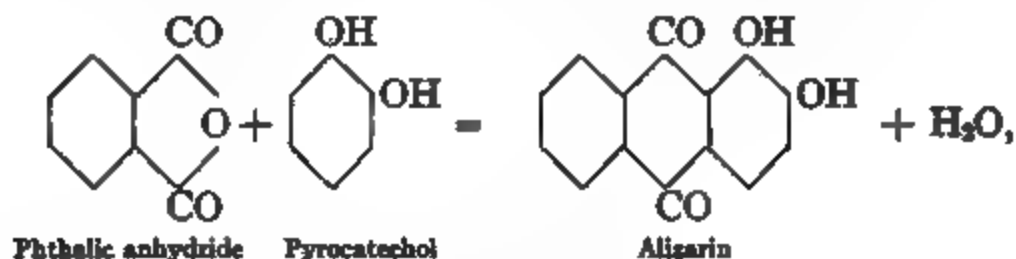
Alizarin crystallizes in red, orthorhombic needles that melt at 289°–290°. It sublimes in orange-red needles. It is only slightly soluble in water, but dissolves readily in organic solvents. In solutions of the caustic alkalis it dissolves with characteristic colors. The concentrated solutions are purplish red, having a purple-blue color by reflected light. On dilution the color changes to a bluish violet.

Alizarin is a mordant dye and gives different colors with different mordants, red with aluminium and tin, violet-black with iron, reddish brown with chromium, and blue with calcium. In dyeing cotton with alizarin (Turkey red dyeing), in order to produce bright red shades with the aluminium mordant, the fabric is treated with Turkey red oil (made by treating castor oil with sulphuric acid and neutralizing the product with soda),

sumac, and precipitated chalk, it having been shown that the presence of calcium is necessary to produce pure red shades.

When distilled with zinc dust alizarin gives anthracene, and it is this reaction that led to the discovery that alizarin is a derivative of anthracene, and to its artificial preparation from that hydrocarbon.

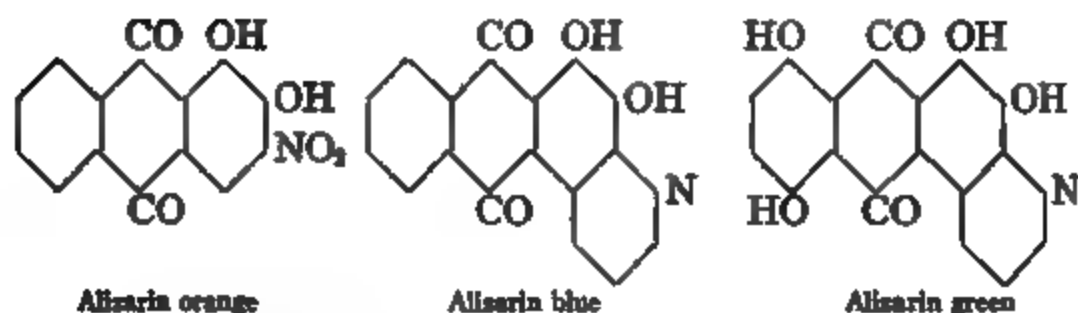
**Constitution of alizarin.** — The preparation of alizarin from anthraquinone- $\beta$ -sulphonic acid and the fact that it gives a diacetate shows that alizarin is a dihydroxyl derivative of anthraquinone. Since it has been made by the oxidation of  $\alpha$ -hydroxyanthraquinone and also by the oxidation of  $\beta$ -hydroxyanthraquinone, the two hydroxyl groups must be in the  $\alpha,\beta$ -positions. Its formation from phthalic anhydride and pyrocatechol by heating with sulphuric acid to  $150^\circ$ ,



proves that both hydroxyl groups are in the same benzene ring and in the ortho position to each other. Hence alizarin is 1,2-dihydroxyanthraquinone. This formula for alizarin is also in accord with the fact that it gives two nitro products (1,2,3 and 1,2,4) and that it gives purpurin, trihydroxyanthraquinone (1,2,4) on oxidation. Purpurin also results from the oxidation of quinizarin (1,4-dihydroxyanthraquinone, formed from phthalic anhydride and hydroquinol), and hence must have the hydroxyl groups in the 1, 2, 4 positions.

**3-Nitroalizarin, alizarin orange**, is made on the large scale by nitrating alizarin, and is a valuable mordant dye. On reduction it gives 3-aminoalizarin. It is also used in making *alizarin blue*.

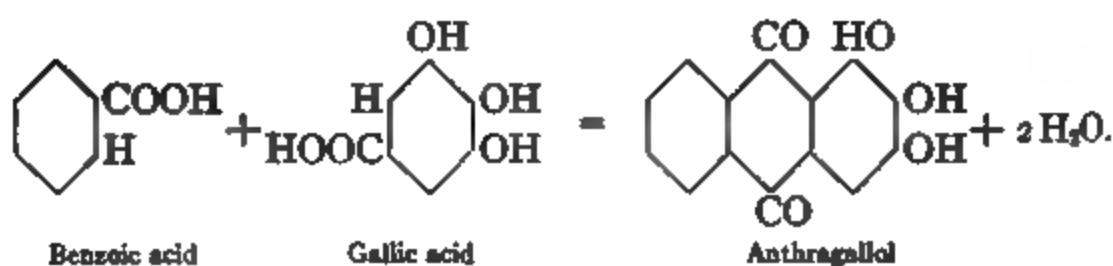
**Alizarin blue** is made by heating alizarin orange, 3-aminoalizarin and glycerol with sulphuric acid (see Skraup's synthesis of quinoline (509)): —



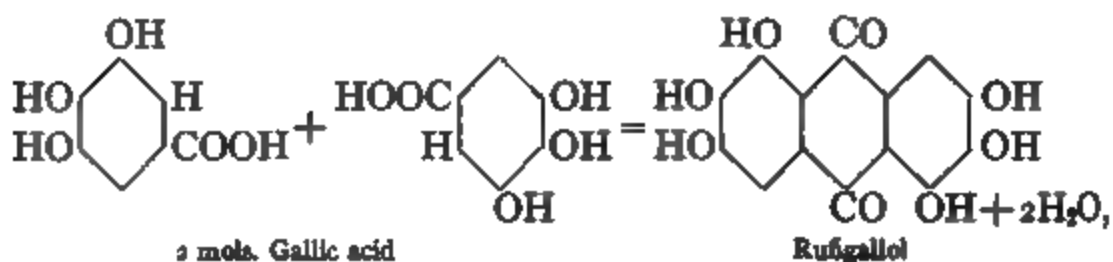
It is a valuable mordant dye. It undergoes oxidation when treated with fuming sulphuric acid to *Alizarin green*. (See formula above.)

**Purpurin**, 1,2,4-trihydroxyanthraquinone, is one of the dyes found in madder root together with alizarin and is, therefore, present in natural alizarin. It can be made from alizarin-4-sulphonic acid by heating with alkalis and also by the oxidation of either alizarin or quinizarin with manganese dioxide and sulphuric acid. Like alizarin it is a valuable mordant dye.

**Anthragallol** (anthracene brown) is 1,2,3-trihydroxyanthraquinone. It is not made from anthraquinone, but by heating gallic acid and benzoic acid with sulphuric acid:—



When gallic acid alone is heated with sulphuric acid it gives hexahydroxyanthraquinone (rufigallol):<sup>1</sup>

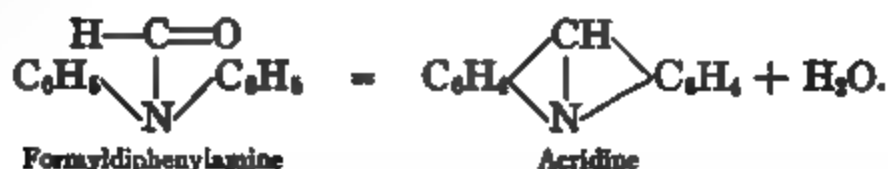


which is also used as a mordant dye.

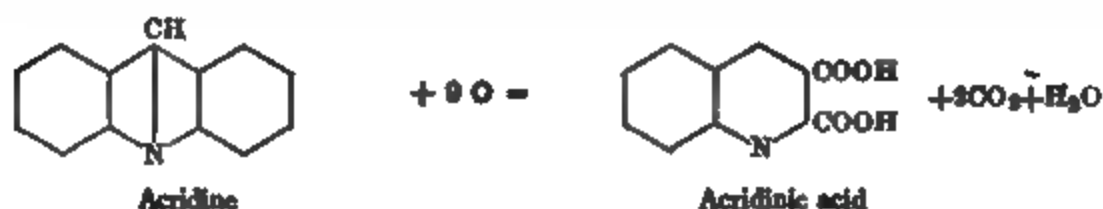
<sup>1</sup> See *Synthetic Dyestuffs*, by J. C. Caine and J. T. Thorpe, for other dyestuffs derived from anthraquinone.

## ACRIDINE

**Acridine**,  $C_{13}H_9N$ , is present in crude anthracene and also in crude diphenylamine. It is formed synthetically by heating diphenylamine and formic acid or formyldiphenylamine with zinc chloride:—

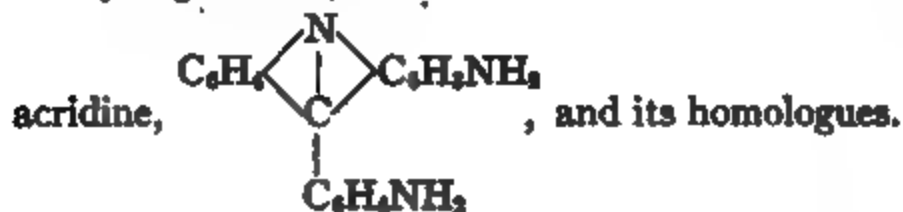


It crystallizes from hot water, in which it is difficultly soluble, in colorless needles. It melts at  $107^\circ$ , sublimes very readily even at  $100^\circ$ , and boils at  $345^\circ$ – $346^\circ$ . It is characterized by the bluish fluorescence of its dilute solutions. On oxidation it gives acridinic acid ( $\alpha,\beta$ -quinolinedicarboxylic acid):—



The constitution of acridine as a derivative of anthracene in which one of the  $\gamma$ -CH groups is replaced by nitrogen follows from the above synthesis and from the fact that it gives acridinic acid on oxidation.

**Chrysaniline** or phosphine, a valuable yellow dye, used largely for dyeing leather, is a mixture of the salts of diaminophenyl-



## PHENANTHRENE

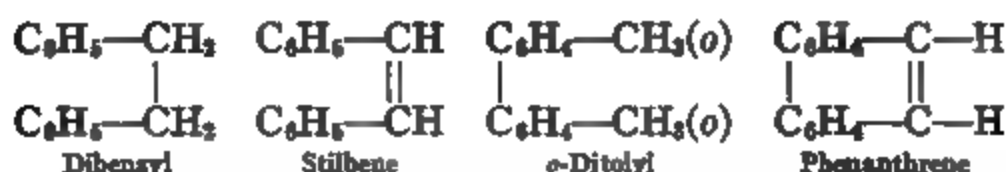
**Phenanthrene**,  $C_{14}H_{10}$ , isomeric with anthracene, is found in anthracene oil and hence in crude anthracene (514). It has been obtained by distilling morphine with zinc dust. It crystallizes from alcohol in colorless, monoclinic leaflets, that melt at  $100.35^\circ$ .



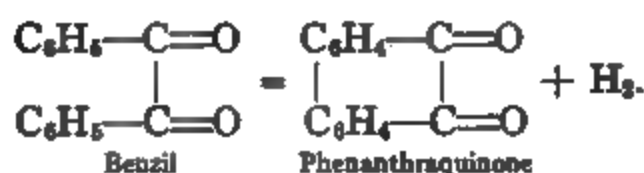
Its boiling point is  $340^{\circ}$  (cor.). It is more readily soluble in alcohol than anthracene and its solutions show a bluish fluorescence. The pure substance is best prepared by the reduction of pure phenanthraquinone (527). Oxidizing agents convert it into phenanthraquinone and into diphenic acid,  $\text{C}_6\text{H}_5\text{—COOH}$  (*o*)

$\begin{array}{c} | \\ \text{C}_6\text{H}_5\text{—COOH} \end{array}$  (*o*), a diorthodicarboxylic acid of diphenyl. It

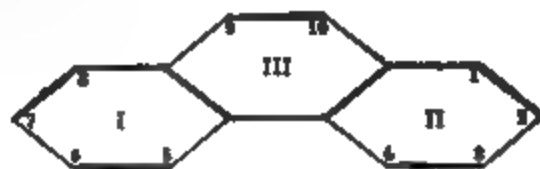
has been made by conducting dibenzyl, stilbene, or *o*-ditolyl through a red-hot tube:—



It will be seen from the above formulas that the change consists in the loss of hydrogen and the union of the residues, as in the formation of diphenyl from benzene and of *o*-ditolyl from toluene. In a similar manner benzil is converted into phenanthraquinone when heated with aluminium chloride:—



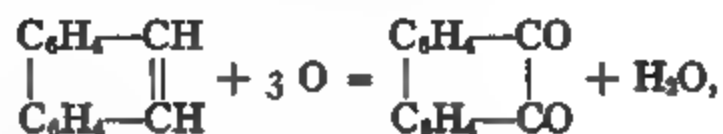
The formation of phenanthrene from stilbene and from *o*-ditolyl, as well as the fact that it gives diphenic acid on oxidation proves that phenanthrene is a derivative of diphenyl, containing a  $\text{—CH=CH—}$  group joined to two ortho carbon atoms, as shown in the formula:—



It will be noted from this formula that phenanthrene contains three benzene rings, and that five monosubstitution products with the same substituent are possible (1, 2, 3, 4, and 9). Five

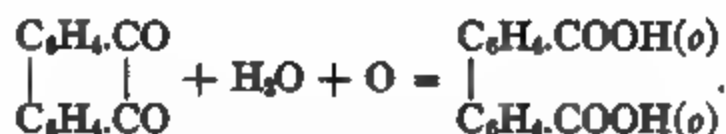
*mononitrophenanthrenes are known.* Phenanthrene is of interest mainly because of its close connection with the very valuable opium alkaloids, morphine, codeine, and thebaine. These alkaloids undoubtedly contain a phenanthrene nucleus. Phenanthrene is at present of little practical importance, though some dyes are made from phenanthraquinone.

Phenanthraquinone is formed by the oxidation of phenanthrene with chromic acid mixture: —



or from benzil (526).

It crystallizes in orange-yellow needles, that melt at 206.5° to 207.5°. It sublimes in orange-red plates. It is somewhat soluble in hot water, more so in alcohol, and in glacial acetic acid. It dissolves in a warm solution of sodium bisulphite, from which it is precipitated by acids or alkalies. This conduct is made use of to separate it from anthraquinone, which is insoluble in a solution of sodium bisulphite. Oxidizing agents convert it into diphenic acid:

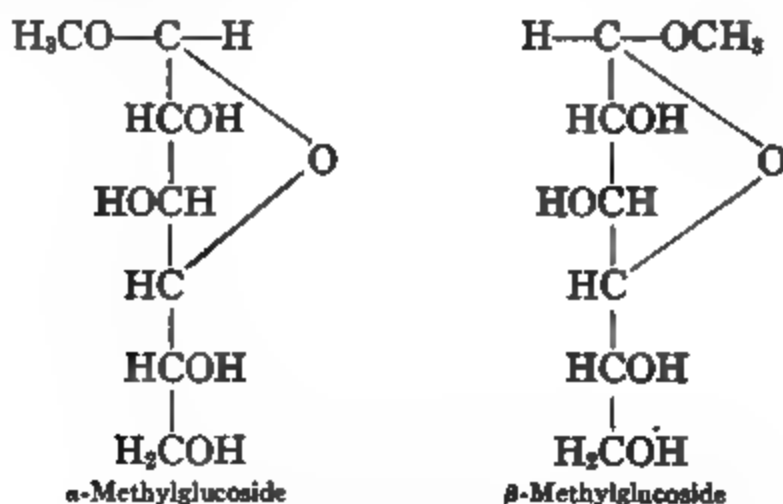


When distilled with zinc dust it is reduced to phenanthrene.

## CHAPTER XXI

### GLUCOSIDES<sup>1</sup>

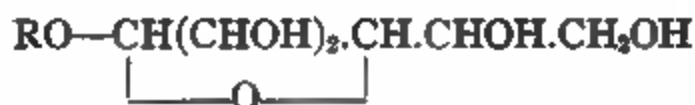
**The Methylglucosides.** — When glucose is dissolved in cold methyl alcohol saturated with dry hydrochloric acid gas, and the solution is allowed to stand for several hours, it is converted into a mixture of  $\alpha$ -methylglucoside and  $\beta$ -methylglucoside, which are separated by fractional crystallization.  $\alpha$ -Methylglucoside melts at  $165^\circ$  and is dextrorotatory ( $+157^\circ$ );  $\beta$ -methylglucoside melts at  $104^\circ$  and is levorotatory ( $-33^\circ$ ). When hydrolyzed the  $\alpha$ -compound yields  $\alpha$ -glucose, and the  $\beta$ -product  $\beta$ -glucose. The rotatory power of these glucosides is the same in a freshly prepared solution as it is in one that has been kept for some time, which is not the case with glucose. The methylglucosides do not give reactions characteristic of the aldehydes. They are regarded as stereoisomeric and have the following formulas: —



It will be noted that the methylglucosides are methyl derivatives of the two stereoisomeric forms of *d*-glucose (221). The only

<sup>1</sup> See E. Frankland Armstrong: *Simple Carbohydrates and Glucosides*, 3d ed. 1919.

difference between them is in the space arrangement of the hydrogen atom and the methoxyl around the upper carbon atom. These synthetic glucosides are completely analogous to the natural glucosides. Like them they are hydrolyzed to glucose and an alcohol by the action of dilute mineral acids or by enzymes. Thus, maltase hydrolyzes the  $\alpha$ - but not the  $\beta$ -compound, and emulsin the  $\beta$ - but not the  $\alpha$ -product, the action of the enzymes being specific. The natural glucosides occur in plants especially in the fruit, roots, and bark and they are accompanied by the enzyme that hydrolyzes them to a sugar (generally *d*-glucose) and an alcohol, aldehyde, phenol, acid, etc. All these glucosides are ethers of glucose having the general formula : —



where R represents the residue of the alcohol, aldehyde, phenol, acid, etc. which may be present. As most of the natural glucosides are hydrolyzed by emulsin, but not by maltase, they are regarded as having a structure similar to that of  $\beta$ -methylglucoside, in which the methyl group is replaced by some other radical. Maltose, which, like  $\alpha$ -methylglucoside, is readily hydrolyzed by maltase but not by emulsin, is an  $\alpha$ -glucoside and has a configuration similar to that of the  $\alpha$ -methylglucoside, a glucose residue taking the place of the methyl group. It has been shown in several cases that the enzyme can effect the synthesis of the compound it hydrolyzes. Thus, a mixture of maltose and isomaltose has been made from glucose by the action of maltase. Invertase, lactase, emulsin and the lipases also act synthetically. The reactions are reversible and stop when equilibrium is established.

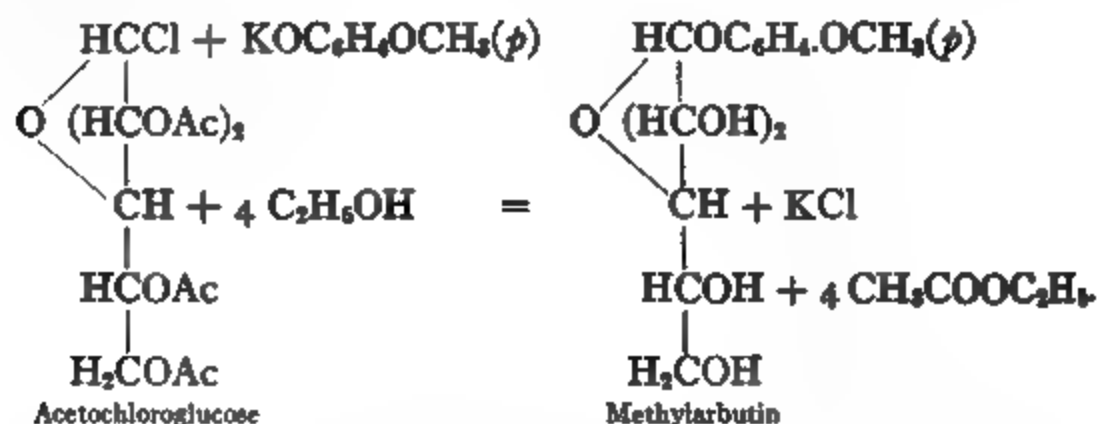
A few of the more important glucosides are given below.

**Aesculin**,  $\text{C}_{15}\text{H}_{18}\text{O}_9 + 1\frac{1}{2} \text{H}_2\text{O}$ , occurs in the bark of the horse-chestnut tree (*Aesculus hippocastanum*) and yields glucose and aesculetin (dihydroxycoumarin) on hydrolysis.

**Amygdalin**,  $\text{C}_{20}\text{H}_{27}\text{O}_{11}\text{N} + 3 \text{H}_2\text{O}$ , is found in bitter almonds, in the leaves of the cherry laurel, and in the kernels of apricots,

peaches, plums, cherries, etc. It is hydrolyzed by mineral acids or by emulsin, an enzyme present in bitter almonds, to benzaldehyde, glucose, and hydrocyanic acid (394).

**Arbutin**,  $C_{12}H_{16}O_7$ , and **methylarbutin**,  $C_{12}H_{18}(CH_3)O_7$ , are both present in the leaves of the bearberry (*Arbutus uva ursi*). They yield glucose and hydroquinol or the monomethyl ether of hydroquinol on hydrolysis. Methylarbutin has been made synthetically by the action of acetochloroglucose on the potassium salt of the monomethyl ether of hydroquinol in alcoholic solution:—



The acetochloroglucose is formed by the action of acetyl chloride on glucose. Both an  $\alpha$ - and a  $\beta$ -acetochloroglucose are now known. It is only the  $\beta$ -compound that gives glucosides, as the  $\alpha$ -product is converted into the  $\beta$ -acetochloroglucose by the action of alkalies.

**Coniferin**,  $C_{18}H_{22}O_8 + 2 \text{H}_2\text{O}$ , is the glucoside found in the conifers. It gives glucose and coniferyl alcohol on hydrolysis, and the latter is converted into vanillin by oxidation. It was used at one time in the preparation of vanillin on the large scale.

**Helicin**,  $C_{18}H_{16}O_7 + \frac{3}{4} \text{H}_2\text{O}$ , does not occur in nature. It is made by the oxidation of salicin (see below) with dilute nitric acid or by the action of  $\beta$ -acetochloroglucose on the potassium salt of salicylic aldehyde in alcoholic solution. It is hydrolyzed by emulsin to glucose and salicylic aldehyde.

**Phloridzin**,  $C_{21}H_{24}O_{10}$ , is found in the root bark of fruit trees. It yields glucose and **phloretin**,  $C_{15}H_{14}O_6$ , when hydrolyzed with acids. Phloretin gives phloretic acid,  $C_9H_{10}O_3$ , and phloro-

glucinol (389) on hydrolysis. Phloridzin has the remarkable power of producing glycosuria when injected subcutaneously.

**Salicin**,  $C_{12}H_{14}O_7$ , occurs in willow bark and also in poplars. It is used in medicine as a remedy for rheumatism and as a febrifuge. It has been made synthetically from  $\beta$ -acetochloroglucose and salicylic alcohol. It is hydrolyzed by emulsin to glucose and salicylic alcohol. When treated with benzoyl chloride it gives a benzoyl derivative in which the benzoyl group is in the glucose residue. This product is identical with the natural glucoside, *populin*, found in the bark of a number of species of poplar (*Populus*).

**Saponins**,  $C_nH_{2n-2}O_{10}$ , form a group of closely related glucosides, widely distributed in nature, whose aqueous solutions froth like soap solutions when shaken. They yield sugars and sapogenin,  $C_{18}H_{22}O_8$ , on hydrolysis.

**Sinigrin**, potassium myronate,  $C_{10}H_{16}O_9NS_2K$ , occurs in black mustard seed. It is hydrolyzed by the enzyme, myrosin, which is also present in the seed, to allyl isothiocyanate (mustard oil), glucose, and monopotassium sulphate:—



A number of important glucosides, such as the tannins, indican, and ruberythric acid have already been mentioned.<sup>1</sup>

The red and blue coloring matters of fruits and flowers are termed *anthocyanins* (Gr. *anthos*, flower, *kuanos*, blue). These anthocyanins are glucosides. They undergo hydrolysis with dilute mineral acids, yielding glucose and the free coloring matters termed *anthocyanidins*. The blue coloring matter of the cornflower is due to the presence of a potassium salt of an anthocyanin. The same anthocyanin is the cause of the red color of the rose and the geranium, in which it is present in the form of a red oxonium salt.

<sup>1</sup> See *Simple Carbohydrates and Glucosides*, by E. F. Armstrong, for the function of the carbohydrates and glucosides in plants.

## CHAPTER XXII

### PLANT ALKALOIDS<sup>1</sup>

THE alkaloids are complex, basic, nitrogenous organic compounds found in plants. Some of them are aliphatic compounds, such as caffeine and theobromine (270), and have already been treated of. Others have been shown to be derived from pyridine, quinoline, or isoquinoline. On account of their physiological action on the animal organism they form an extremely important class of compounds and many of them constitute the *active principles* of the common vegetable drugs used in medicine. Almost all the plants yielding alkaloids belong to the class of *dicotyledons*, and it is seldom that the plant contains only one alkaloid. Generally several are present and they are chemically and often physiologically closely related. Alkaloids rarely occur in plants in the free condition, but almost always combined with acids in the form of salts. The acids with which they are combined are those usually found in plants, oxalic, malic, succinic, citric, tannic, etc., or special acids characteristic of the plant (quinic acid with the quinine alkaloids, meconic acid with the opium alkaloids, aconitic acid with aconite alkaloids). A few of the alkaloids contain only carbon, hydrogen, and nitrogen and are liquid, volatile compounds, *e.g.* *conine* and *nicotine*; most of them, however, contain oxygen in addition to the above named elements and are crystalline, non-volatile bases. They are nearly all optically active and usually levorotatory. A few like *conine* are secondary bases, but most of them are tertiary amines. Some like *betaine* (251) are inner ammonium salts. The alkaloids are precipitated from solutions of their salts by certain *alkaloid reagents*, such as tannic acid and phosphomolybdic acid, gold and platinum chlorides, a solution of iodine in potassium iodide, a solution of potassium mercuric

<sup>1</sup> See *The Plant Alkaloids*, by T. A. Henry, 1913.

iodide, etc. They are also generally characterized by their bitter, astringent taste and physiological action. Many of them give characteristic color reactions with chlorine water, nitric or sulphuric acids, etc. which serve to identify them.

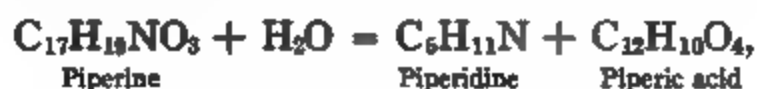
The alkaloids are usually isolated from the plants by extraction with alcohol or water, in which their salts occurring in plants are generally soluble. When they occur in the form of salts insoluble in these solvents, the ground plant is mixed with lime or magnesia and then extracted with some solvent in which the base is soluble. They are then purified by recrystallization.

Only a few of the more important alkaloids derived from pyridine, quinoline or isoquinoline will be dealt with here.

#### ALKALOIDS DERIVED FROM PYRIDINE

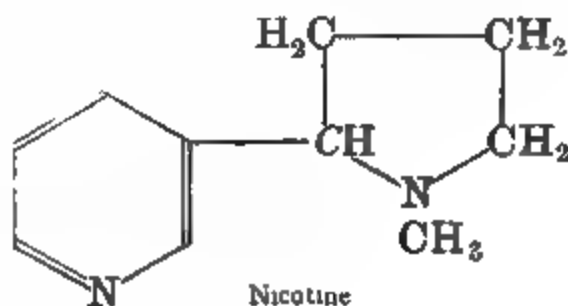
*Conine* (442) and *piperidine* (441) have already been presented.

**Piperine**,  $C_{17}H_{19}NO_3$ , is found in the fruits of black and white pepper (*Piper nigrum*). It gives piperidine and piperic acid on hydrolysis:—



and has been made synthetically from the chloride of piperic acid and piperidine, hydrochloric acid being eliminated. Hence piperine is piperylpiperidine,  $C_6H_{10}N.C_{12}H_9O_3$ . Both piperidine and piperic acid have been made synthetically.

**Nicotine**,  $C_{10}H_{14}N_2$ , is the principal alkaloid found in tobacco leaves (*Nicotiana tabacum*), in which it occurs in combination with citric and malic acids. It is a colorless, oily base which rapidly turns brown in the air and is extremely poisonous. Its solution in water is levorotatory and it is a ditertiary base. On oxidation with potassium permanganate it gives nicotinic acid ( $\beta$ -pyridinecarboxylic acid (440)) and hence it is a  $\beta$ -derivative of pyridine. It has been made synthetically and shown to be  $\beta$ -pyridyl- $\alpha$ -N-methylpyrrolidine:—

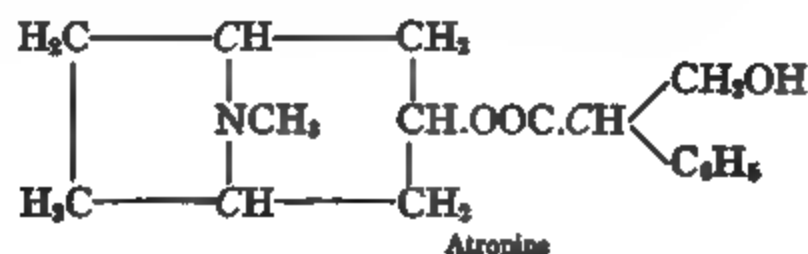




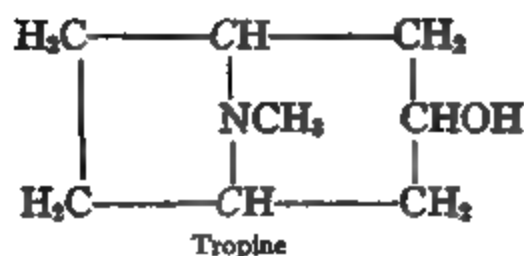
## SOLANACEOUS ALKALOIDS

Only three of these alkaloids are used in medicine, atropine, hyoscyamine, and scopolamine. They are characterized by their mydriatic action, that is, their power of dilating the pupil of the eye when the aqueous solutions of their salts are dropped into the eye.

**Atropine**,  $C_{17}H_{23}NO_3$ , is seldom found in plants. It is made from its stereoisomer, *hyoscyamine*, by the action of dilute alkalis. Hyoscyamine is the chief constituent of *Atropa belladonna*, *Datura stramonium*, *Hyoscyamus*, etc. It crystallizes from dilute alcohol in needles (m. p.  $108.5^\circ$ ), and is levorotatory. Its sulphate,  $(C_{17}H_{23}NO_3)_2 \cdot H_2SO_4$ , is readily soluble in water, has a bitter taste, and a neutral reaction. Like atropine it causes dilation of the pupil of the eye. It is readily converted into its racemic modification, atropine, by treating its alcoholic solution with a small quantity of alkali; this is the commercial method of preparing atropine. Atropine crystallizes in colorless prisms (m. p.  $115.5^\circ$ ). The aqueous solution is bitter to the taste, has an alkaline reaction and is optically inactive. The sulphate,  $(C_{17}H_{23}NO_3)_2 \cdot H_2SO_4 + H_2O$ , is the salt generally used in medicine. It is principally used owing to its property of causing dilation of the pupil of the eye, and this property may be used for its detection. A drop or two of an aqueous solution, 1 part of atropine in 130,000 parts of water, when introduced into the eye of a cat is sufficient to produce this effect. The formula for both atropine and hyoscyamine is represented thus:—



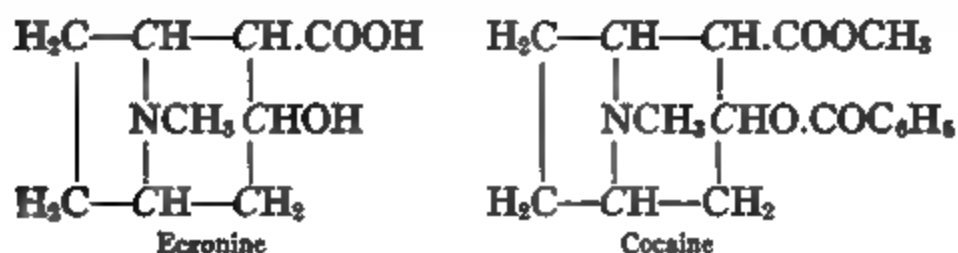
It will be seen from this formula that atropine is an ester of atropine with the acid,  $C_6H_5 \cdot CH < \begin{smallmatrix} \text{CH}_2\text{OH} \\ \text{COOH} \end{smallmatrix}$ , called tropic acid.



Both tropine and tropic acid have been made synthetically.

### COCA ALKALOIDS

**Cocaine**,  $\text{C}_{17}\text{H}_{21}\text{NO}_4$ , is the most important of the alkaloids found in coca leaves (*Erythroxylon coca*). Its hydrochloride,  $\text{C}_{17}\text{H}_{21}\text{NO}_4 \cdot \text{HCl}$ , is used in surgery as a local anæsthetic. The base crystallizes from alcohol in prisms (m. p.  $98^\circ$ ), is soluble in hot water and is levorotatory. The aqueous solution is alkaline to litmus and produces the characteristic numbness when applied to the tongue. When hydrolyzed with acids or alkalis cocaine gives ecgonine, benzoic acid, and methyl alcohol, and is therefore the methyl ester of benzoylecgonine. Ecgonine has been shown to be tropinecarboxylic acid:—



It is obtained by the hydrolysis of the residues found in coca leaves, after extracting the cocaine, and is converted into cocaine by first benzoylating it with benzoic anhydride, and then methylating the benzoylecgonine in alkaline solution with methyl iodide.

Like morphine cocaine is a habit-forming drug.

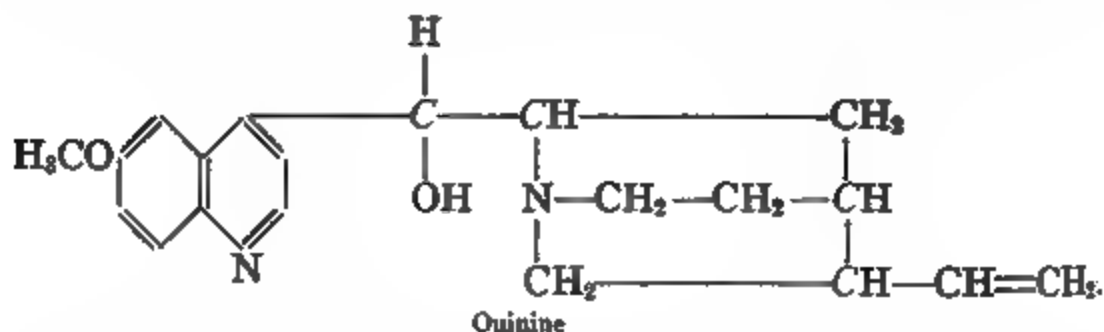
### ALKALOIDS DERIVED FROM QUINOLINE

#### *Cinchona Alkaloids*

**Quinine**,  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 + 3 \text{H}_2\text{O}$ , is the most important of all the alkaloids. It occurs together with cinchonine and other alkaloids in the bark of cinchona trees indigenous to South

America. Most of the cinchona bark now comes from the island of Java and from Bengal, where the trees are grown in Government plantations. The world's annual production of quinine sulphate,  $(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 + 8 H_2O$ , is over 250,000 kilograms. It is largely used as a specific for malaria and as a prophylactic against this disease. It is also used as a febrifuge and as a tonic.

Quinine crystallizes in needles melting at  $57^\circ$  or when anhydrous at  $177^\circ$ . It is a strong ditertiary, diacid base, has an intensely bitter taste, and is levorotatory. The neutral sulphate in dilute solution shows a blue fluorescence, which is characteristic. The following formula has been assigned to quinine:—



and is in accord with the following facts: Quinine is an unsaturated compound, it combines with two atoms of hydrogen to form hydroquinine, and with two of bromine to form a dibromide. This is believed to be due to the presence of the vinyl group,  $-CH=CH_2$ . Quinine is converted into a ketone, quinone,  $C_{20}H_{22}N_2O_2$ , on oxidation, and hence must contain a secondary alcohol group. With stronger oxidizing agents it gives quininic acid (*p*-methoxyquinoline- $\gamma$ -carboxylic acid), which shows that it is a *p*-methoxy derivative of quinoline, and that the second half of the molecule replaces the  $\gamma$ -hydrogen of quinoline. Fusion with alkalis gives *p*-methoxyquinoline from the first half of the molecule, and  $\beta$ -ethylpyridine from the second half.

**Cinchonine**,  $C_{19}H_{21}(OH)N_2$ , is also present in cinchona bark and resembles quinine in its physiological action, but is weaker. It is derived from quinine by replacing the methoxyl group by hydrogen. It also gives a ketone, cinchoninone,  $C_{19}H_{20}ON_2$ , on oxidation, showing the presence of the secondary alcohol

group, and with stronger oxidizing agents, cinchoninic acid ( $\gamma$ -quinolinecarboxylic acid). When fused with caustic potash it gives quinoline and  $\beta$ -ethylpyridine. Like quinine it is unsaturated and forms a crystalline dibromide.

#### STRYCHNOS ALKALOIDS

**Strychnine**,  $C_{21}H_{22}O_2N_2$ , and **brucine**,  $C_{21}H_{26}O_4N_2$ , both occur in the seeds of *Strychnos nux vomica*. Strychnine crystallizes in colorless rhombohedra that melt at  $268^\circ$ . It is slightly soluble in water, more so in alcohol and readily in chloroform. It is levorotatory. The aqueous solution has an alkaline reaction and an extremely bitter taste, one part in 700,000 parts of water being recognizable by the bitter taste. The nitrate, sulphate and hydrochloride are used in medicine, principally as a tonic. On account of its poisonous properties strychnine is frequently used to exterminate rodents and other vermin.

Although strychnine contains two nitrogen atoms it acts as a monacid base. When fused with caustic potash it yields both quinoline and indol, and when distilled with sodalime, carbazole. Hence strychnine must contain residues both of quinoline and carbazole. Its structural formula is not yet known.

**Brucine** is strychnine with two hydrogens replaced by two methoxy groups. It is less poisonous than strychnine.

#### ALKALOIDS DERIVED FROM ISOQUINOLINE

**Morphine**,  $C_{17}H_{19}NO_3 + H_2O$ , is the most important of the opium alkaloids, and the first alkaloid ever isolated. Opium is the sun-dried latex of the unripe fruit of the opium poppy (*Papaver somniferum*) and has been used for centuries. Twenty-five alkaloids have been isolated from opium, but the only ones used in medicine are morphine and its methyl ether, codeine. Morphine crystallizes from alcohol in colorless, triclinic prisms containing a molecule of water of crystallization. It melts with decomposition at  $254^\circ$ , has a bitter taste and is sparingly soluble in most solvents. The salt most commonly used in medicine is the sulphate,  $(C_{17}H_{19}NO_3)_2H_2SO_4 + 5 H_2O$ . In small doses

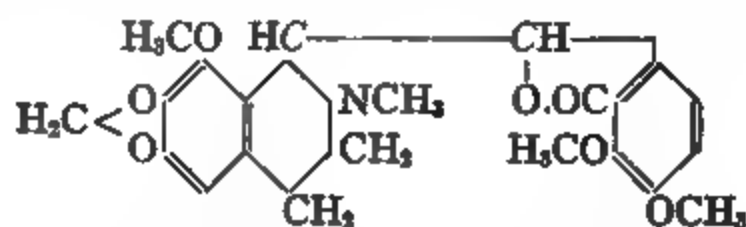
it acts as a sedative, producing sleep and relieving pain. It is a habit-forming drug. In doses of 0.2 to 0.3 gram it is fatal to **MURIL**

Although a large amount of work has been done on morphine and its derivatives, its structural formula has not yet been clearly established. On distillation with zinc dust it gives phenanthrene. It contains two hydroxyl groups, as with acetic anhydride it gives a diacetate, *heroin*, used in medicine. Of the two hydroxyl groups one acts as a phenol group, as morphine is soluble in a solution of caustic alkali and gives the methyl ether, *codeine*, insoluble in alkali, when methylated. The second hydroxyl is present in the form of a secondary alcohol group, as codeine,  $C_{18}H_{21}NO_3$ , gives a ketone, codeinone,  $C_{18}H_{19}NO_3$ , on oxidation.

Codeine is made on the large scale by methylating morphine in alkaline solution with dimethyl sulphate. It resembles morphine in its physiological action, but is less narcotic.

Over 600,000 pounds of opium valued at \$5,387,855 were imported into the United States in 1920.

**Narcotine,  $C_{22}H_{22}NO_7$ .**—When opium is extracted with water to obtain morphine, etc., most of the narcotine remains in the insoluble residue from which it is extracted with dilute hydrochloric acid. It crystallizes from alcohol in colorless needles (m. p.  $176^\circ$ ). It is levorotatory and is a weak monacid, tertiary base. In its physiological action it resembles codeine, but is less depressant. It is much less poisonous than either morphine or codeine. It is little used in medicine. It has been made synthetically and shown to have the following formula:—



It will be noted that it is a derivative of tetrahydroisoquinoline and that it contains three methoxy groups and a lactone ring.

## THE PROTEINS

The nitrogenous, organic substances found in living matter and produced by it are called proteins (Gr. *proteios*, the first). Like the fats and carbohydrates they are found only in living matter or in the products of the action of living matter. The food of animals consists of proteins, fats, and carbohydrates, and of these the proteins are the most important. An animal can exist for a long time without fats or carbohydrates, but it dies when deprived of proteins. The proteins are also essential constituents of all living cells and are therefore of the first importance for the phenomenon of life. They are absolutely necessary for the growth and development of living cells. They consist of carbon, hydrogen, nitrogen, oxygen, and some sulphur. Sometimes they contain phosphorus. The amount of these constituents varies somewhat in the different proteins and is approximately C—50 per cent, H—7 per cent, N—16 per cent, O—25 per cent, S—0.2 to 3 per cent, P—0 to 3 per cent. Those which are soluble in water form colloidal solutions and do not diffuse through parchment paper, and this fact is taken advantage of to free them from salts and crystalloids. These solutions are levorotatory. Most of the proteins are amorphous substances without a definite melting point, that carbonize on heating and give off gas. Some have been obtained crystalline, *e.g.*, the albumins, hæmoglobin, edestin from hemp seed, etc.

Many of the proteins can be "salted out" from their aqueous solutions by sodium chloride or magnesium sulphate, and almost all of them are precipitated unchanged by saturating their solutions with ammonium sulphate. Alcohol also precipitates proteins unchanged from aqueous solutions, while strong alcohol coagulates them. Heat coagulates the proteins, and the temperature at which coagulation takes place is characteristic for the different proteins. These coagulated proteins can be brought into solution again by the action of dilute acids or alkalis, but these solutions are no longer coagulable by heat. They are called metaproteins and are precipitated by neutralizing their solutions. The proteins are also precipitated by copper sulphate, ferric

chloride, mercuric chloride, etc., and by the alkaloid precipitating agents, especially phosphotungstic acid. They give certain color reactions, which are used as tests for proteins, such as:—

1. *The biuret reaction* (284).
2. *Millon's reaction*. This consists in the formation of a red color when a protein is heated with a mixture of mercuric nitrate and nitrite (Millon's reagent).
3. *Xanthoproteic reaction*. Most proteins develop a yellow color when heated with nitric acid. This changes to an orange when the solution is made alkaline.

Chemically most of the proteins have weak acid and basic properties, like the amino acids. They are digested by certain enzymes and hydrolyzed by mineral acids to mixtures of amino acids. They are regarded as composed of residues of these amino acids combined with one another in the same way as in the polypeptides (271). These polypeptides give many of the reactions characteristic of the proteins, and several of them have been found among the products of the hydrolysis of the proteins. Little is known regarding the molecular weight of the proteins except that it must be very large. Determinations of the osmotic pressure of solutions of the albumin of the hen's egg, for example, have given results which point to a molecular weight of about 12,000 for that substance. The percentage of iron in haemoglobin, assuming that the molecule contains one atom of iron, indicates a molecular weight of about 16,500 for this substance.

The following classification of the proteins has been adopted by the American Society of Biochemists:<sup>1</sup>—

Proteins are defined as nitrogenous, organic substances consisting wholly, or in part, of amino acids, united by their carboxyl and amino groups. They are divided into three main classes:—

1. Simple proteins,
2. Compound or conjugated proteins,
3. Derived proteins.

The first two classes are natural proteins; the last includes the artificial proteins and proteins modified by reagents.

<sup>1</sup> See p. 112, *Physiological Chemistry*, by A. P. Mathews, 3d ed., 1921. /

**I. The simple proteins.**—These are proteins occurring in nature which when treated with enzymes or acids break down, yielding only  $\alpha$ -amino acids or their derivatives. They differ from the conjugated proteins in that the latter not only break down into  $\alpha$ -amino acids but also into other non-protein substances. The simple proteins are separated into the following groups by their solubilities and other properties.

*A. Albumins.* Simple proteins, coagulable by heat, soluble in water and dilute salt solutions. *Ovalbumin, serum albumin.*

*B. Globulins.* Simple proteins, coagulable by heat, insoluble in water, but soluble in dilute solutions of salts of strong bases and acids. *Serum globulin, edestin.*

*C. Glutelins.* Simple proteins, coagulable by heat, insoluble in water or dilute salt solutions, but soluble in very dilute acids or alkalies. *Glutenin* of wheat.

*D. Prolamines.* Simple proteins, insoluble in water, soluble in 80 per cent alcohol. *Gliadin, hordein, zein.* Found in cereals.

*E. Albuminoids.* Simple proteins, insoluble in dilute acid, alkali, water or salt solutions. *Elastin, keratin, collagen.*

*F. Histones.* Simple proteins, not coagulable by heat, soluble in water and in dilute acid; strongly basic, and insoluble in ammonia. *Histone* from birds' corpuscles and from thymus.

*G. Protamines.* Simple proteins, strongly basic, non-coagulable by heat, soluble in ammonia and yielding large amounts of diamino acids on hydrolysis. *Sturin, salmin, clupein.* Found in ripe sperm of fishes.

**II. Conjugated proteins.**—These are compounds of simple proteins with some other non-protein group. The other group is generally acid in nature. They are subdivided into the following classes:—

*A. Hæmoglobins.* The prosthetic group (Gr. *prosthesos*, additional) is colored. It may be hematin as in hæmoglobin or the colored radicals of phycoerythrin or phycocyan. *Hæmoglobin, hæmocyanin, phycoerthrin, phycocyan.*

*B. Glucoproteins.* The prosthetic group contains a carbohydrate radical. In mucin and cartilage it may be chondroitic acid. *Mucin, ichthulin, mucoids.*



**C. Phosphoproteins.** Proteins of the cytoplasm. The prosthetic group is not known. It contains phosphoric acid, but not in the form of nucleic acid or a phospholipin. *Casein, vitellin.*

**D. Nucleoproteins.** Proteins of the nucleus. The chromatin. The prosthetic group is nucleic acid. *Nuclein, nucleo-histone.*

**E. Lecithoproteins.** Found in the cytoplasm and limiting membrane. The prosthetic group is lecithin or a phospholipin. No lecithoprotein has yet been isolated. They probably exist.

**III. Derived proteins.** — This group is an artificial one. It includes all the various cleavage products of the proteins occurring in nature, which are produced by the action of reagents or enzymes, or physical agents, such as heat; and also artificially synthesized proteins. It is divided into various groups according to solubility and also somewhat according to the degree of hydrolysis.

**A. Primary Protein Derivatives.**

**a. Proteans.** Derived proteins. The first products of the action of acids, enzymes or water on simple proteins. Insoluble in water. *Edestan, myosan.*

**b. Metaproteins.** The further action of acids and alkalis produces metaproteins. These are soluble in weak acids or alkalis, but insoluble in neutral solutions. *Acid albumin, (acid metaprotein); alkali albumin.*

**c. Coagulated proteins.** Insoluble protein products produced by the action of heat or alcohol.

**B. Secondary Protein Derivatives.**

**a. Proteoses.** Hydrolytic cleavage products of proteins. Soluble in water, not coagulable by heat, precipitated by saturating their solutions with ammonium sulphate.

**b. Peptones.** Hydrolytic cleavage products of proteins; soluble in water, not coagulable by heat, not precipitated by saturation with ammonium sulphate. Generally diffusible and giving the biuret reaction.

**c. Peptides.** These are compounds of the amino acids, of which the composition is known. Many are synthetic. The amino acids are united through the amino and carboxyl groups.

may or may not give the biuret reaction. They are not labile by heat. They are called di-, tri-, tetra-, pentales, etc., according to the number of residues of amino contained in the molecule. (See Polypeptides (271).) For details concerning these substances the student is referred to books on Physiological Chemistry.

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